

# PATENT ABSTRACTS OF JAPAN

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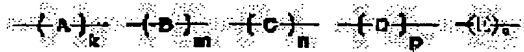
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ASATAKE ATSUSHI

## (54) RECORDING PAPER FOR INK JET PRINTER AND RECORDING METHOD

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To prevent the deterioration of picture quality, the degradation of a drying property, the occurrence of cracks, and the formation of whisker-like stripes generated at a boundary between the printed part and the non-printed part by containing inorganic minute grains having a combined organic cathionic polymer in the receptor layer.

**SOLUTION:** The inorganic minute grains are ones having a minute grain diameter, in particular, they are preferable to be aluminum oxide, colloidal silica, amorphous silica, zinc oxide, and titanium oxide. Although the configuration of these inorganic minute grains is not limited in particular, it is preferable to be a globular shape, cube, rod, needle, chain, annular shape, and a plate. The average grain diameter is preferable to be in the range of about 1-500 nm. These inorganic minute grains are combined with an organic cathionic polymer and the weight ratio of the organic cathionic polymer relative to the inorganic minute grains (an organic cathionic polymer/inorganic minute grains) is preferable to be in the range of 1/99 or more and 99/1 or less and, more preferably, in the range of 10/90 or more and 90/10 or less and, particularly preferably, in the range of 20/80 or more and 80/20 or less.



## LEGAL STATUS

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[Date of final disposal for application]

[Patent number]

[Date of registration]

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rejection]

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[Date of extinction of right]

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CLAIMS

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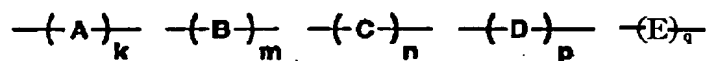
[Claim(s)]

[Claim 1] The record form for ink jet printers characterized by containing the non-subtlety particle which the organic cationic polymer combined in the acceptance layer.

[Claim 2] The record form for ink jet printers according to claim 1 characterized by said organic cationic polymer consisting of compounds expressed with the following general formula (I).

[Formula 1]

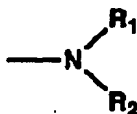
一般式 (I)



In a general formula (I), (A) expresses the monomeric unit which carried out the polymerization of the monomer which has quaternary ammonium, and which can be copolymerized, and (B) expresses the monomeric unit which carried out the polymerization of the monomer which is contained at least one of the structures expressed with the following general formula (II), (III), (IV), and (V), and which can be copolymerized.

[Formula 2]

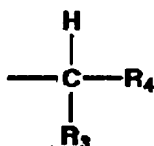
一般式 (II)



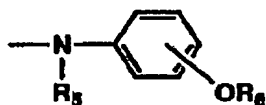
一般式 (III)



一般式 (IV)



一般式 (V)



In a general formula (II), R1 and R2 express an aliphatic series radical, and Z expresses a nonmetal atom group required to form 5 members or a six membered ring in collaboration with  $-C=N=C-$  in a general formula (III). In a general formula (IV), R3 and R4 express an aromatic series radical, a halogen atom, a cyano group, and an oxy-carbonyl group. In a general formula (V), R5 expresses a hydrogen atom and an aliphatic series radical, and R6 expresses an aliphatic series radical. In the above-mentioned general formula (I), (C) expresses the monomeric unit which carried out the polymerization of the monomer which has at least two ethylene-like unsaturated bond radicals, and which can be copolymerized, and (D) expresses the monomeric unit which carried out the polymerization of (A), (B), and the monomer in which the copolymerization of those other than (C) is possible. In the above-mentioned general formula (I), the monomeric unit expressed with (E) expresses the monomeric unit which has the radical which can form said non-subtlety particle and covalent bond. Ten to 95-mol%, in m, zero to ten-mol%, p expresses zero to 80-mol %, and, as for q, n expresses [ k ] 0.1 to 20-mol % zero to 30-mol%. However, the sum total of k, m, n, p, and q is 100-mol %.

[Claim 3] The record form for ink jet printers according to claim 1 or 2 with which the organic cationic polymer weight ratio (an organic cationic polymer / non-subtlety particle) to said non-subtlety particle is characterized by or more 1/99 being 99/1 or less.

[Claim 4] The record form for ink jet printers according to claim 1 to 3 with which the non-subtlety particle which said organic cationic polymer combined is characterized by containing ten to 99% of the weight in an acceptance layer.

[Claim 5] The record form for ink jet printers given in any of claims 1-4 characterized by a base material being polyolefine coat paper.

[Claim 6] The color ink jet record approach characterized by what is recorded on a record form according to claim 1 to 5 with the recording device outputted using five or more sorts of different ink.

[Claim 7] The color ink jet record approach characterized by what is recorded on a record form according to claim 1 to 5 to at least one sort of criteria colors with the recording device recorded in two or more sorts of different ink.

[Claim 8] The color ink jet record approach according to claim 7 characterized by what is recorded with the recording apparatus which said criteria color records in two or more sorts of ink in which the absorbances of the ink of this criteria color differ substantially.

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[Translation done.]

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the record form for ink jet printers and the record approach applicable to various kinds of ink jet printer methods.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the record form for ink jet printers and the record approach applicable to various kinds of ink jet printer methods.

[0002]

[Description of the Prior Art] Ink jet recording apparatus (in this description, it is also called an ink jet printer.) However, of course, this invention is applicable to the recording device at large which is not limited to the so-called printer. There is little noise, and since it is also easy to perform multicolor record by using two or more ink nozzles possible [ high-speed printing ], it has spread quickly as an image information output unit for computers especially in recent years.

[0003] Moreover, there are some ink jet printers which were developed for full color record and which can output an image [ high definition like it is equal to the color picture of a film photo method ]. Moreover, the content of the image to output is also expanded to a color block copy, a design image, etc. as which the image quality near a photograph is required from an alphabetic character, a graphic form, etc.

[0004] therefore, as the record medium, it rubs from the coat paper and the regular paper of glossiness or concentration which become low — carry out — the glossy paper or the gloss film using the resin coat paper out of which the opaque film which has the glossiness more near a photograph, and gloss come — or many cast-coated papers which carried out the cast of the front face of coat paper, and gave specular-gloss nature have come to be used.

[0005] It corresponds to these and using the water-soluble polymer which swells or dissolves water color ink as an ink absorbing layer (or coat layer) is proposed. For example, in JP,62-263084,A, the acceptance layer in which a mean molecular weight contains [ the record sheet for ink jet printers which it dries by the cold dry cleaning method once the acceptance layer formed from the gelatin water solution of Specification pH makes the gel state the gelatin applied in JP,6-64306,A, and is obtained ] 5x104 or more polyethylene oxide by JP,62-214985,A is proposed, respectively.

[0006] Moreover, by one side, the acceptance layer of the porosity mold using a non-subtlety particle is proposed. The acceptance layer of a porosity mold prepares a detailed opening by the particle, and receives ink, and drying is dramatically excellent and has the advantage that there is also little color muddiness and it can output the image of high resolution.

[0007] It cannot respond with the advent of a high speed and a multi-discharge quantity ink jet printer, but color muddiness (bleeding) and beading (Pacific cod) produce a print rate and ink absorption capacity between dots, and it is becoming impossible however, to obtain a quality image in recent years. Furthermore, since these printers have realized many gradation by using shade ink, the amount of ink increases, by the high-humidity condition, poor desiccation especially occurs frequently, and they are posing a serious problem. Although there is the approach of thickening thickness of an acceptance layer as a means to increase absorption capacity in order to solve these problems, poor conveyance arises conversely, or it leads to a cost rise, and is not desirable. Furthermore, since the porosity mold acceptance layer used the non-subtlety particle, the film reinforcement of the acceptance layer itself was high, and it turned out that it also has the trouble

of being easy to produce a crack (crack) since distraction nature is low.

[0008] These troubles pose a still bigger problem, when applying as an object for roll printers. For example, although there is a service bureau which creates a poster etc. as a field which uses a roll printer, since increasing the amount of ink and usually using it with the color-balance adjustment means called RIP in order to improve the sharp nature and contrast of an alphabetic character is generally used, what it is further easy to generate from the desktop mold printer by which an amateur user uses the above problems is the actual condition. Since it is twisted to the shape of a roll strongly also as a product gestalt, it is easy to be generated, and if a crack is printed by the part, the problem on which outflow and image quality deteriorate [ ink ] in the shape of a mustache along with a crack will produce it. Moreover, since it rounds off and is kept after printing for a long period of time, if drying deteriorates, since most users will imprint at the rear face, they have a possibility of spoiling quality. The actual condition is being unable to use him, if a pro user's is most and the user who uses a roll printer does not solve these problems.

[0009]

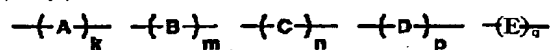
[Problem(s) to be Solved by the Invention] The object of this invention is to offer the record form for ink jet printers and the record approach of solving degradation (beading, bleeding, etc.) of the image quality produced by the high speed and multi-discharge quantity printer which were mentioned above, and which are increasing quickly in recent years, or the roll printer, drying degradation, and generating of the muscle of the shape of a mustache produced on generating of a crack, or the boundary of the printing section and the non-printed section.

[0010]

[Means for Solving the Problem] The above-mentioned technical problem of this invention is the record form for ink jet printers characterized by containing the non-subtlety particle which the organic cationic polymer combined in 1. acceptance layer, and the record form for ink jet printers of said one publication characterized by 2. aforementioned organic cationic polymer consisting of compounds expressed with the following general formula (I), [0011]

[Formula 3]

一般式 (I)



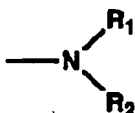
[0012] In a general formula (I), (A) expresses the monomeric unit which carried out the polymerization of the monomer which has quaternary ammonium, and which can be copolymerized, and (B) expresses the monomeric unit which carried out the polymerization of the monomer which is contained at least one of the structures expressed with the following general formula (II), (III), (IV), and (V), and which can be copolymerized.

[0013]

[Formula 4]



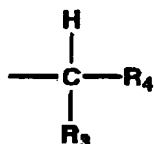
一般式 (II)



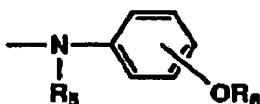
一般式 (III)



一般式 (IV)



一般式 (V)



[0014] In a general formula (II), R1 and R2 express an aliphatic series radical, and Z expresses a nonmetal atom group required to form 5 members or a six membered ring in collaboration with  $\text{---C=N=C---}$  in a general formula (III). In a general formula (IV), R3 and R4 express an aromatic series radical, a halogen atom, a cyano group, and an oxy-carbonyl group. In a general formula (V), R5 expresses a hydrogen atom and an aliphatic series radical, and R6 expresses an aliphatic series radical.

[0015] In the above-mentioned general formula (I), (C) expresses the monomeric unit which carried out the polymerization of the monomer which has at least two ethylene-like unsaturated bond radicals, and which can be copolymerized, and (D) expresses the monomeric unit which carried out the polymerization of (A), (B), and the monomer in which the copolymerization of those other than (C) is possible.

[0016] In the above-mentioned general formula (I), the monomeric unit expressed with (E) expresses the monomeric unit which has the radical which can form said non-subtlety particle and covalent bond.

[0017] Ten to 95-mol%, in m, zero to ten-mol%, p expresses zero to 80-mol %, and, as for q, n expresses [ k ] 0.1 to 20-mol % zero to 30-mol%. However, the sum total of k, m, n, p, and q is 100-mol %.

[0018] 3. Record Form for Ink Jet Printers of Said 1 or 2 Publications to which Organic Cationic Polymer Weight Ratio (Organic Cationic Polymer / Non-Subtlety Particle) to Said Non-Subtlety Particle is Characterized by or More 1/99 being 99/1 or Less, 4. The record form for ink jet printers given in either [ to which the non-subtlety particle which said organic cationic polymer combined is characterized by containing ten to 99% of the weight in an acceptance layer / said ] 1-3, 5. with the recording device outputted to said any of 1-4 which are characterized by a base material being polyolefine coat paper using the record form for ink jet printers of a publication, and 6.5 or more sorts of different ink the color ink jet record approach characterized by what is

recorded on a record form given in either [ said ] 1-5, and 7. — to at least one sort of criteria colors with the recording device recorded in two or more sorts of different ink The color ink jet record approach characterized by what is recorded on a record form given in either [ said ] 1-5, 8. Said criteria color is attained by each of color ink jet record approach \*\* of said seven publications characterized by what is recorded with the recording apparatus recorded in two or more sorts of ink in which the absorbances of the ink of this criteria color differ substantially.

[0019]

[Embodiment of the Invention] This invention is further explained to a detail. The non-subtlety particle which the organic cationic polymer first used for this invention combined is explained.

[0020] The non-subtlety particle used for this invention is a particle which has a detailed particle size, for example, a kaolin (clay), talc, titanium oxide, a zinc oxide, a zirconium dioxide, cerium oxide, an oxidization yttrium, the tin oxide, an antimony oxide sol, a niobium oxide sol, an aluminum silicate, an aluminum hydroxide, an aluminum oxide, a calcium silicate, a magnesium silicate, colloidal silica, or amorphous silica is mentioned.

[0021] An aluminum oxide, colloidal silica, amorphous silica, a zinc oxide, and titanium oxide are especially mentioned preferably in these. Although there is especially no limit in the configuration of these inorganic particle, the shape of a globular form, a cube form, a cylinder, a needle, and a chain, annular, plate-like, etc. are mentioned preferably. As mean particle diameter, the range of 1-500nm is desirable.

[0022] These non-subtlety particles are combined by the organic cationic polymer described below, it is or more 10/90 or less 90/10 range that it is or more 1/99 99/1 or less range desirable still more preferably, and the weight ratio (an organic cationic polymer / non-subtlety particle) of an organic cationic polymer to a non-subtlety particle is or more 20/80 80/20 or less range especially preferably.

[0023] The non-subtlety particle which the organic cationic polymer combined in this invention is in the condition that the reaction radical which can be connected with a non-subtlety particle in an organic cationic polymer means the thing in the condition of being selectively combined with the non-subtlety particle, and is covered preferably (these particles may be called a polymer joint inorganic particle below).

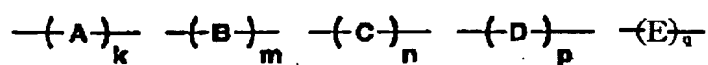
[0024] Next, the organic cationic polymer used in this invention is explained.

[0025] The organic cationic polymer used in this invention has the unit expressed with the following desirable general formulas (I).

[0026]

[Formula 5]

一般式 (I)

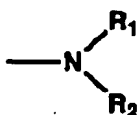


[0027] In a general formula (I), (A) expresses the monomeric unit which carried out the polymerization of the monomer which has quaternary ammonium, and which can be copolymerized, and (B) expresses the monomeric unit which carried out the polymerization of the monomer which is contained at least one of the structures expressed with a general formula (II), (III), (IV), and (V), and which can be copolymerized.

[0028]

[Formula 6]

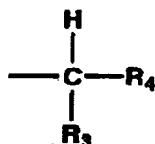
一般式 (II)



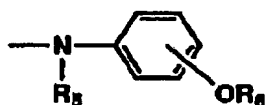
一般式 (III)



一般式 (IV)



一般式 (V)



[0029] In a general formula (II), R1 and R2 express an aliphatic series radical, and Z expresses a nonmetal atom group required to form 5 members or a six membered ring in collaboration with  $-C-N=C-$  in a general formula (III). In a general formula (IV), R3 and R4 express an aromatic series radical, a halogen atom, a cyano group, and an oxy-carbonyl group. In a general formula (V), R5 expresses a hydrogen atom and an aliphatic series radical, and R6 expresses an aliphatic series radical.

[0030] In the above-mentioned general formula (I), (C) expresses the monomeric unit which carried out the polymerization of the monomer which has at least two ethylene-like unsaturated bond radicals, and which can be copolymerized, and (D) expresses the monomeric unit which carried out the polymerization of (A), (B), and the monomer in which the copolymerization of those other than (C) is possible.

[0031] In the above-mentioned general formula (I), the monomeric unit expressed with (E) expresses the monomeric unit which has the non-subtlety particle used for this invention, and the radical which can form covalent bond.

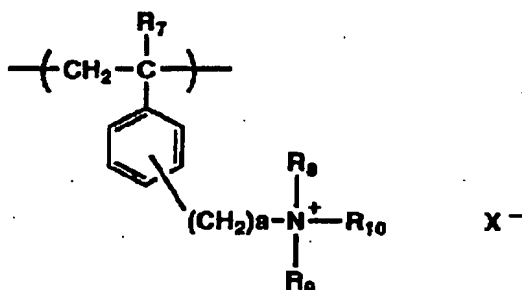
[0032] Ten to 95-mol%, in m, zero to ten-mol%, p expresses zero to 80-mol %, and, as for q, n expresses [ k ] 0.1 to 20-mol % zero to 30-mol%.

[0033] In the above-mentioned general formula (I), the monomeric unit of (A) expressed with the following general formulas (VI), (VII), and (VIII) (IX) is desirable.

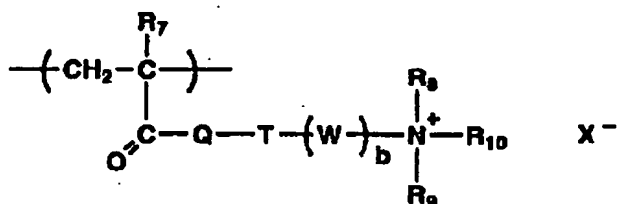
[0034]

[Formula 7]

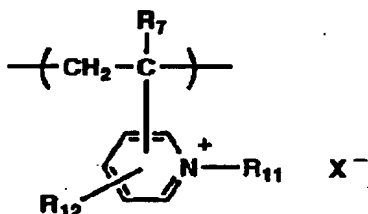
一般式 (VI)



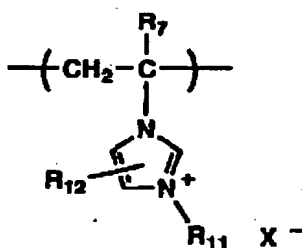
一般式 (VII)



一般式 (VIII)



一般式 (IX)



[0035] In the above-mentioned general formula (VI), (VII), and (VIII) (IX), R7 expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R7, a hydrogen atom or a methyl group is desirable.

[0036] In the above-mentioned general formula (VI), (VII), and (VIII) (IX), R8, R9, R10, and R11 express the aliphatic series radical (they are a KISHIRU radical, benzyl, etc. to a methyl group, an ethyl group, and cyclo) of the carbon atomic numbers 1-10. Even if mutually the same, you may differ, and it may join together mutually, and the substituent expressed with these [ R8, R9 and R10 ] may form cyclic structure. It is a methyl group, an ethyl group, and benzyl preferably as R8, R9, and R10, and a methyl group and especially benzyl are desirable.

[0037] In the above-mentioned general formula (VI), (VII), and (VIII) (IX), X expresses an anion, for example, halogen ion (for example, a chloride ion, bromine ion, iodine ion, etc.), alkyl-sulfuric-acid ion (for example, methylsulfuric acid ion etc.), alkyl or aryl sulfonic-acid ion (for example, methansulfonic acid ion, p-toluenesulfonic-acid ion, etc.), acetic-acid ion, etc. are mentioned. Among these, halogen ion and especially alkyl-sulfuric-acid ion are desirable.

[0038] In the above-mentioned general formula (VI), a expresses the integer of 1 to 4.

[0039] In the above-mentioned general formula (VII), Q expresses an oxygen atom or a nitrogen atom. T and W express the connection radical of bivalence, for example, express a xylene radical, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-, and a phenylene group to ethylene, 1, and 4-cyclo. b expresses 0 or 1.

[0040] In the above-mentioned general formula (VIII) and (IX), R12 expresses radicals, such as a

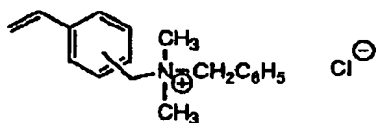
hydrogen atom, aliphatic series radicals (for example, a methyl group, t-butyl, etc.), aromatic series radicals (for example, phenyl group etc.), a halogen atom, a cyano group, acyl groups (for example, an acetyl group, benzoyl, etc.), oxy-carbonyl groups (for example, methoxycarbonyl group etc.), aminocarbonyl radicals (for example, aminocarbonyl radical etc.), and a nitro group.

[0041] In the above-mentioned general formula (I), the instantiation compound of a monomer led to the monomeric unit expressed with (A) is shown below.

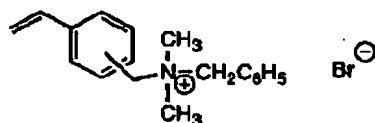
[0042]

[Formula 8]

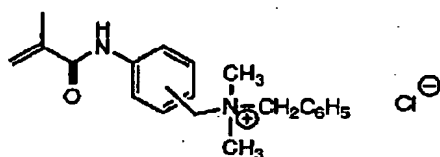
(A-1)



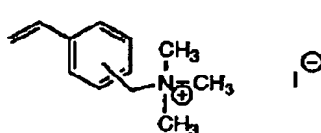
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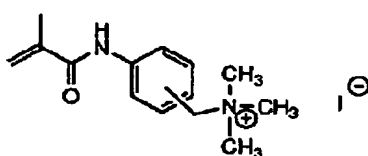
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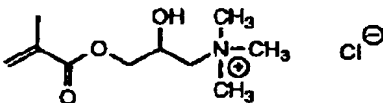
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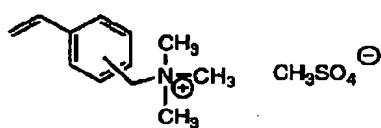
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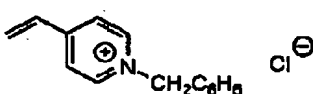
(A-6)



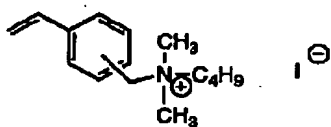
(A-7)



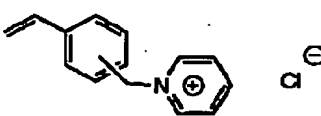
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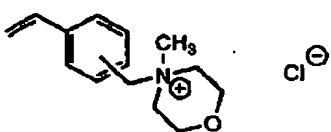
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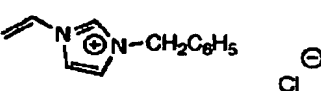
(A-10)



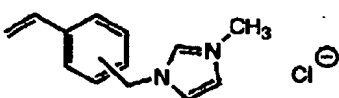
(A-11)



(A-12)



(A-13)

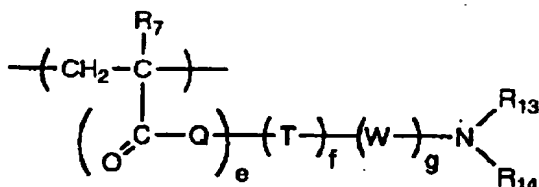


[0043] In the above-mentioned general formula (I), the following general formulas (X), (XI), and (XII) the monomeric unit of (B) expressed are desirable.

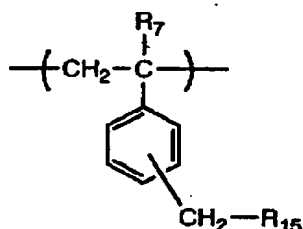
[0044]

[Formula 9]

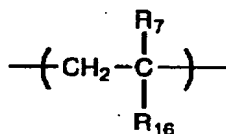
一般式 (X)



一般式 (XI)



一般式 (XII)



[0045] the above-mentioned general formula (X) and (XI) — and (XII) it sets and R7 expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R7, a hydrogen atom or a methyl group is desirable.

[0046] In the above-mentioned general formula (X), Q expresses an oxygen atom or a nitrogen atom. T and W express the connection radical of bivalence, for example, express ethylene, 1, 4-cyclo hexylene radical,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ ,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ , and a phenylene group. e, f, and g express 0 or 1, respectively (however, when e is 1, neither f nor g is 0). R13 and R14 express a hydrogen atom, an alkyl group, and an aryl group. The alkyl group and aryl group which are expressed with these [ R13 and R14 ] may join together mutually, and may form cyclic structure.

[0047] In the above-mentioned general formula (XI), R15 expresses a halogen atom (for example, chlorine atom), an aromatic series radical (for example, phenyl group), an aryloxy group (for example, phenoxy group), a hydroxy group, etc.

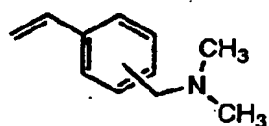
[0048] In the above-mentioned general formula (XII), R16 expresses 2-pyridyl radical, 4-pyridyl radical, and 1-imidazole radical.

[0049] In the above-mentioned general formula (I), the instantiation compound of a monomer led to the monomeric unit expressed with (B) is shown below.

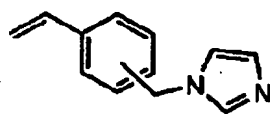
[0050]

[Formula 10]

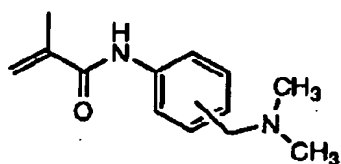
B-1



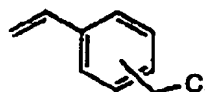
B-2



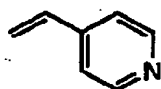
B-3



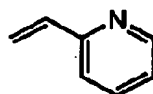
B-4



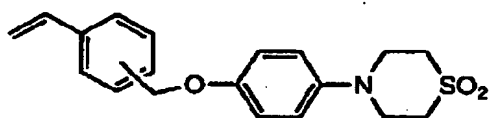
B-5



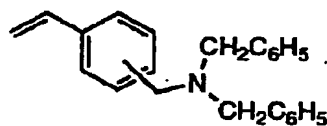
B-6



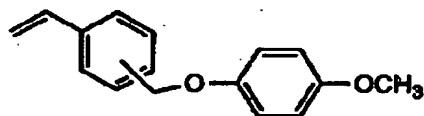
B-7



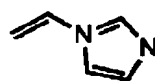
B-8



B-9



B-10



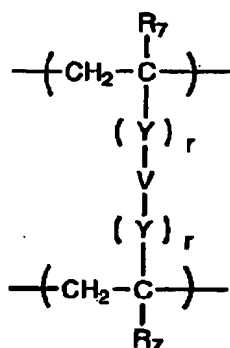
[0051] In the above-mentioned general formula (I), a divinylbenzene, ethylene glycol methacrylate, ethylene glycol acrylate, hydroquinone methacrylate, hydroquinone acrylate, an ethylene JIMETA krill amide, ECHIRENJI acrylamide, etc. are mentioned as a monomer led to the monomeric unit expressed with (C).

[0052] In the above-mentioned general formula (I), the monomeric unit of (C) expressed with the following general formulas (XIII) is desirable.

[0053]

[Formula 11]

一般式 (XIII)



[0054] In the above-mentioned general formula (XIII), R<sub>7</sub> expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R<sub>7</sub>, a hydrogen atom or a methyl group is desirable. Moreover, V expresses the connection radical of bivalence, for example, expresses arylene radicals (for example, a phenylene group, a naphthylene radical, etc.) and alkylene groups (for example, a methylene group, 1, 4-butylene radical, etc.). Y expresses an ester bond (for example, -C(=O)-O-, -O-C(=O)-), amide association (for example, -C(=O)-NH-, -NH-C(=O)-, -SO<sub>2</sub>-NH-), ether linkage (-O-), etc., and r expresses 0 or 1.

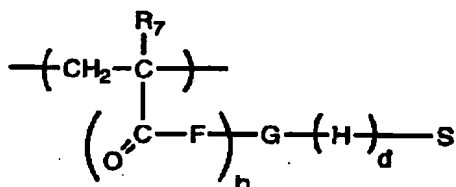
[0055] In the above-mentioned general formula (I), ethylene, a propylene, 1-butene, isobutene, styrene, alpha methyl styrene, vinyltoluene, an acrylic acid and its ester or amide derivatives (for example, a methyl acrylate, butyl acrylate, t-butyl acrylamide, etc.), a methacrylic acid and its ester or amide derivatives (for example, a methyl methacrylate, methacrylic-acid benzyl, n-butyl methacrylamide, etc.), acrylonitrile, a methacrylonitrile, etc. are mentioned as a monomeric unit expressed with (D), for example.

[0056] In the above-mentioned general formula (I), the monomeric unit of (E) expressed with the following general formulas (XIV) is desirable.

[0057]

[Formula 12]

一般式 (XIV)



[0058] In the above-mentioned general formula (XIV), R<sub>1</sub> expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R<sub>1</sub>, a hydrogen atom or a methyl group is desirable. F expresses -O- or -N(R)- (the inside R of a formula expresses a hydrogen atom, an alkyl group, or an aryl group), and b expresses 0 or 1.

[0059] In the above-mentioned general formula (XIV), G and H express the connection radical of bivalence, for example, a methylene group, ethylene, 1, 4-cyclo hexylene radical, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O-, a phenylene group, etc. are mentioned. d expresses the integer of 0, or 1-3.

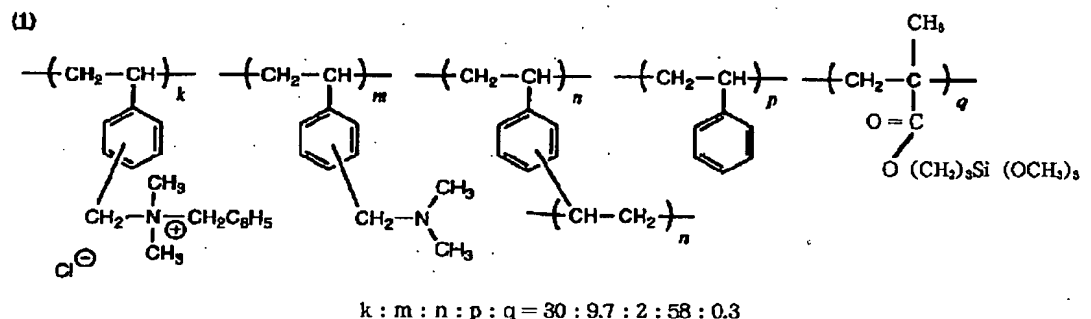
[0060] In the above-mentioned general formula (XIV), S can mention the radical which expresses the non-subtlety particle used for this invention, and the radical which can form covalent bond, for



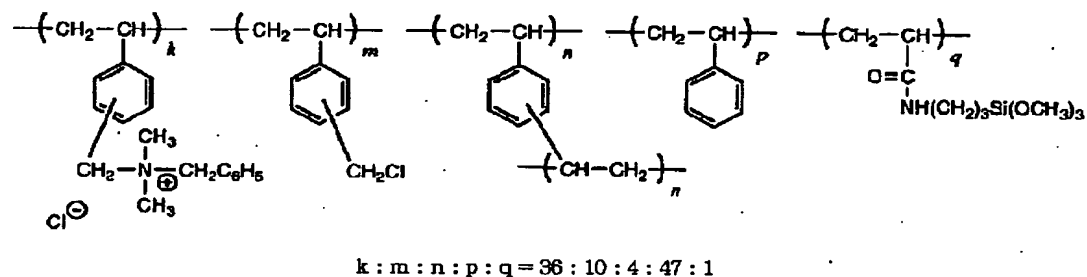
example, is expressed with  $-\text{SiX}_3$ . (X expresses radicals, such as halogen atom (for example, chlorine atom),  $-\text{OR}$  (R expresses acyloxy radicals, such as alkoxy group [ , such as a hydrogen atom, a methoxy group, and an ethoxy radical, ], acetoxy radical, and benzyloxy radical, among formula), and  $-\text{NRR}'$  (R and R' expresses aryl groups, such as alkyl groups, such as a hydrogen atom, a methyl group, and t-butyl, and a phenyl group, among a formula), among a formula.) Although the instantiation compound of an organic cationic polymer used in this invention is shown below, this invention is not limited to this. In addition, the illustrated polymer includes the following repeat unit at a following rate, respectively.

[0061]

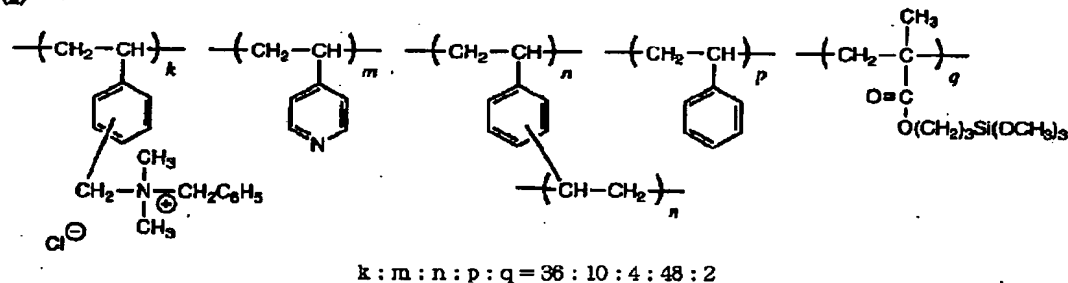
[Formula 13]



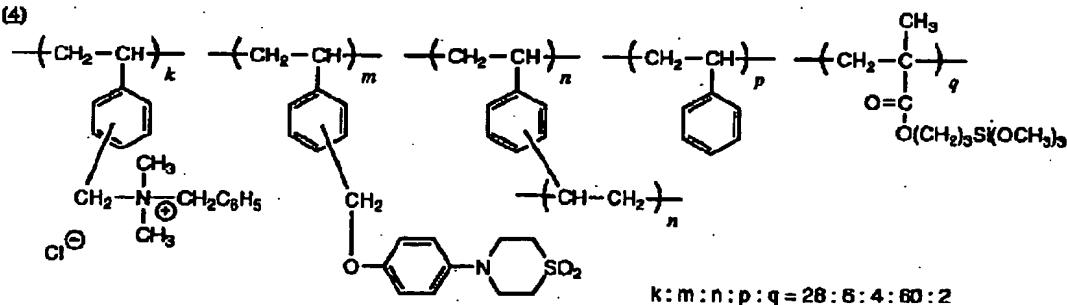
(2)



(3)

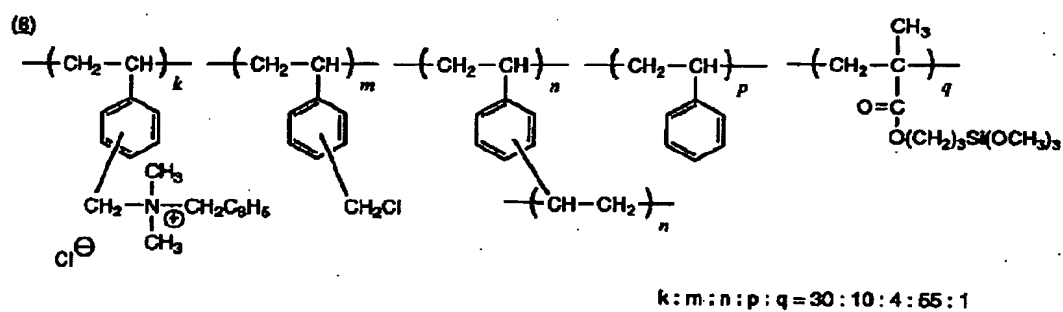
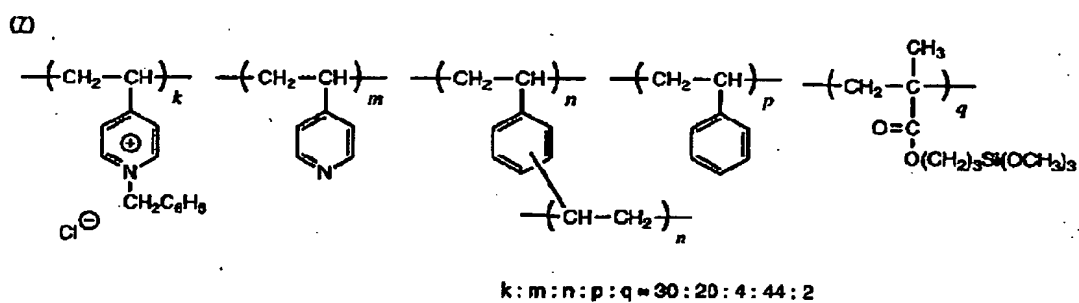
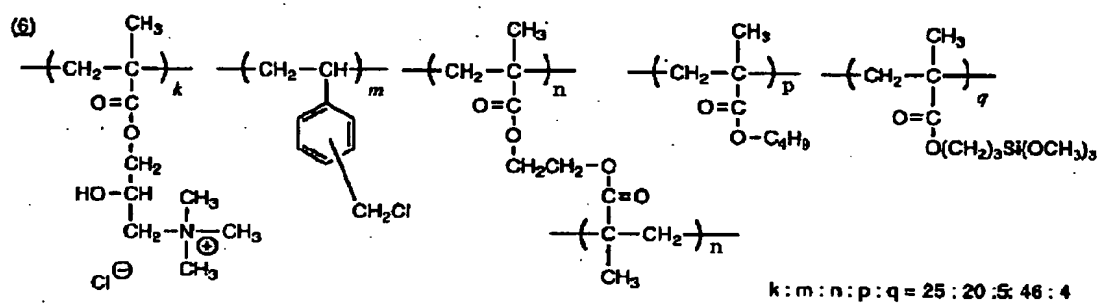
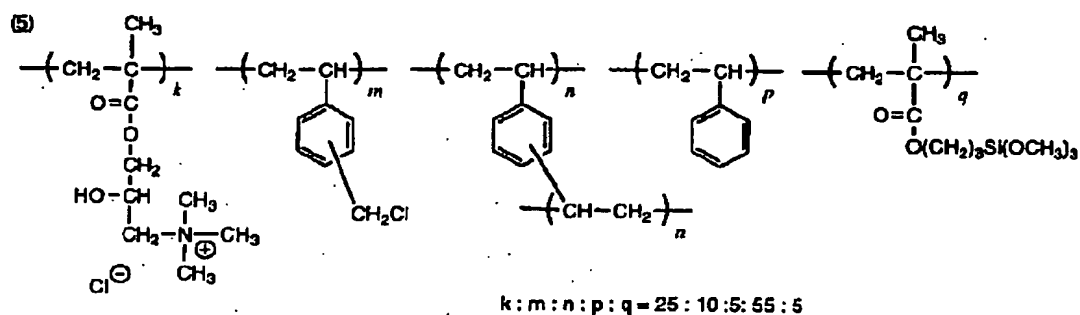


(4)



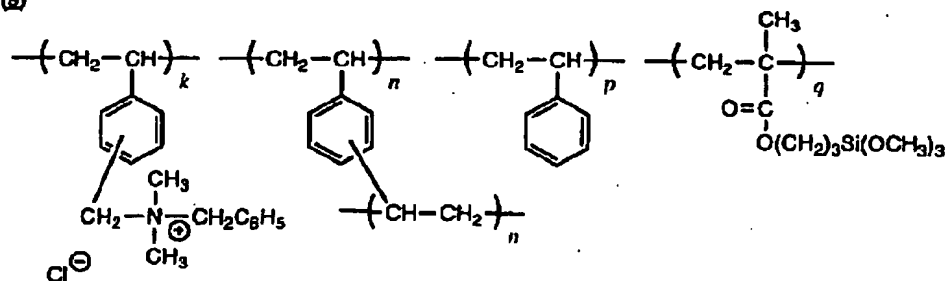
[0062]

[Formula 14]



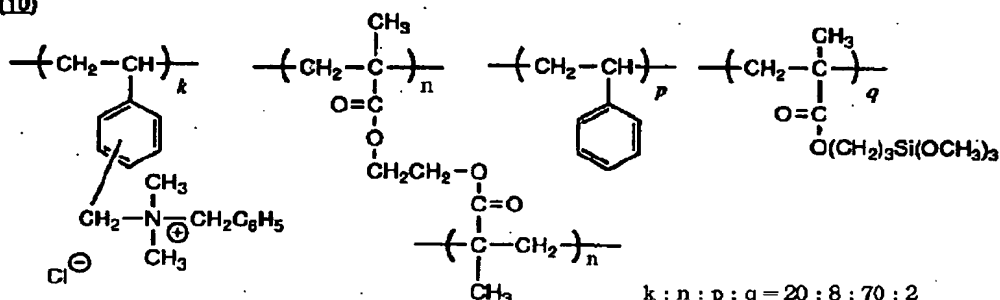
[0063]  
[Formula 15]

(9)



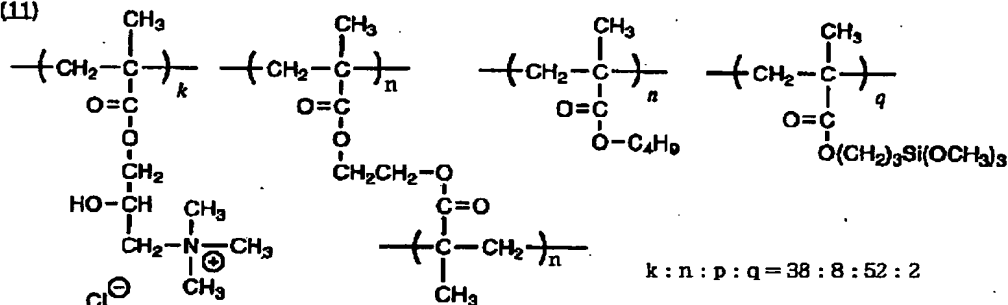
$$k : n : p : q = 30 : 6 : 62 : 2$$

(10)



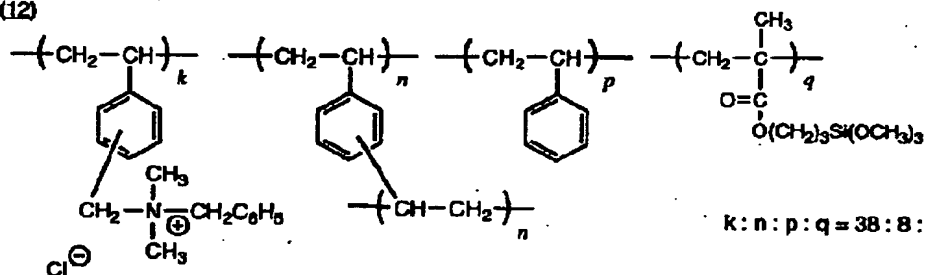
$$k : n : p : q = 20 : 8 : 70 : 2$$

(11)



$$k : n : p : q = 38 : 8 : 52 : 2$$

(12)



$$k : n : p : q = 38 : 8 : 52 : 2$$

[0064] The non-subtlety particle which the organic cationic polymer used in this invention combined For example, the polymerization initiation radical is introduced on the (1) non-subtlety particle front face compoundable by the next approach. The copolymerization nature machine or the chain transfer radical is introduced on the approach of combining by performing a polymerization reaction on a front face, and the (2) non-subtlety particle front face. The approach of combining by performing a polymerization reaction on a front face and the polymerization initiator of (3) cationicity are made to stick to up to a non-subtlety particle front face. The approach of combining by performing a polymerization reaction near the front face and hydrophilic macromere with (4) vinyl groups are made to stick to up to a non-subtlety particle front face. the

approach of combining by performing a polymerization reaction on a front face, and (5) — the approach of combining with a non-subtlety particle, since the organic polymer which introduced the coupling agent into the polymer beforehand is compounded etc. These approaches are explained to the report of for example, the Society of Fiber Science and Technology, Japan, the 49th volume, the report of a 130–136–page publication and a front face, the 28th volume, and a 285–298–page publication etc. at the detail.

[0065] next, the water-soluble binder preferably used by this invention — and — or gelatin is explained.

[0066] Although either can be used if it is gelatin which used the collagen of an animal as the raw material as gelatin preferably used for this invention, the gelatin which used as the raw material a pig skin, oxbone, and the collagen that used the cow bone as the raw material is more desirable. Although there is especially no limit as a class of gelatin, furthermore, liming gelatin, acid-treatment gelatin and derivative gelatin (for example, JP,38-4854,B —) 39-5514, 40-12237, 42-26345, A U.S. Pat. No. 2,525,753 number, said 2,594,293 numbers, said 2,614,928 numbers, said — No. 2,763,639 — said — No. 3,118,766 — said — No. 3,132,945 — said — No. 3,186,846 — said — No. 3,312,553 and British JP,861,414,B — said — the derivative gelatin of a publication can be used for No. 103,189 etc. combining independent or them. If acid-treatment gelatin is used, it is advantageous especially in respect of a water resisting property.

[0067] As an amount of coating of the gelatin contained in the acceptance layer of this invention, 3 – 20 g/m<sup>2</sup> is 5 – 15 g/m<sup>2</sup> desirable still more preferably as solid content.

[0068] As a water-soluble polymer preferably used by this invention, for example, polyvinyl alcohol vinyl formals, such as polyvinyl pyrrolidones, polyvinyl pyridinium halide, and various denaturation polyvinyl alcohol, and the derivative (JP,60-145879,A —) of those 60-220750, 61-143177, 61-235182, Refer to 61-235183, 61-237681, and 61-261089, Polyacrylamide, the poly dimethyl acrylamide, poly dimethylamino acrylate, Sodium polyacrylate, an acrylic-acid methacrylic-acid copolymer salt, polymethacrylic acid soda, the polymer (JP,60-168651,A —) containing acrylic radicals, such as an acrylic-acid vinyl alcohol copolymer salt To 62-9988 etc., a publication, starch, oxidization starch, carboxyl starch, Dialdehyde starch, cation-ized starch, a dextrin, sodium alginate, Gum arabic, casein, a pullulan, a dextran, methyl cellulose, naturally-occurring-polymers ingredients, such as ethyl cellulose, a carboxymethyl cellulose, and hydroxypropylcellulose, or the derivative (JP,59-174382,A —) of those 60-262685, 61-143177, 61-181679, To 61-193879, 61-287782, etc., a publication, a polyethylene glycol, A polypropylene glycol, polyvinyl ether, polyglycerin, A maleic-acid alkyl vinyl ether copolymer, a maleic-acid-N-vinyl pyrrole copolymer, Synthetic polymers (it indicates to JP,61-32787,A, 61-237680, 61-277483, etc.), such as a styrene maleic anhydride copolymer and polyethyleneimine, etc. can be mentioned. They are polyvinyl pyrrolidones, polyvinyl alcohol, and polyalkylene oxide preferably among these polymers.

[0069] As the above-mentioned polyvinyl alcohol, polymerization degree is desirable especially desirable and the range of 200–4000 is 1000–3000.

[0070] The compound shown by the above-mentioned polyalkylene oxide, for example, polyethylene oxide and polyethylene glycols, polypropylene glycols, or the following general formula (P) is mentioned.

[0071] General formula (P)

$R_3O-(A_4-O)_j$  — among  $4-(A_5-O)_j5-(A_6-O)_j6-R_4$  type, although  $A_4$ ,  $A_5$ , and  $A_6$  express the straight chain which is not permuted [ a permutation and ] or the alkylene group of branching, respectively, they do not become the same [ all ] even if  $R_3$  and  $R_4$  are the same respectively — you may differ — a hydrogen atom — the alkyl group which is not permuted [ a permutation and ], an aryl group, an acyl group, etc. are expressed, respectively.

[0072] As each substituent, a hydroxy group, a carboxy group, a sulfonyl group, an alkoxy group, a carbamoyl group, and a sulfamoyl group are mentioned. Preferably,  $R_3$  and  $R_4$  are hydrogen atoms, and  $A_4$ ,  $A_5$ , and  $A_6$  are non-permuted things, respectively. Moreover, as most desirable thing,  $A_4$ ,  $A_5$ , and  $A_6$  are  $-CH_2CH_2-$  or  $-CH(CH_3)-CH_2-$ .

[0073]  $j_4$ ,  $j_5$ , and  $j_6$  express the integer of 0, or 1–500, respectively. However, it is  $j_4+j_5+j_6 \geq 5$ .

[0074] As a thing desirable at polyalkylene oxide, it is polyethylene oxide, it is the polyethylene glycol (PEG may be called) which has average molecular weight in the range of 10,000–500,000

desirable especially preferably, and average molecular weight is the thing of the range of 50,000–300,000.

[0075] The average molecular weight of the above-mentioned polyalkylene oxide is the molecular weight computed with the hydroxyl value.

[0076] In this invention, it is desirable to apply a cross linking agent in the range which does not influence this invention as an object which constructs a bridge in a water-soluble polymer. As a concrete example of a cross linking agent, the aldehyde system compound like formaldehyde and glutaraldehyde, Diacetyl, the ketone compound like a KURORU 2,4-pentanedione, a screw (2-chloro ethylurea), 2-hydroxy – Triazine system compounds, such as 4 and 6-dichloro-1,3,5-triazine, The compound which has a reactant halogen like a U.S. Pat. No. 3,288,775 number publication, A divinyl sulfone, a carbamoyl pyridinium system compound given in JP,8-50342,A, A compound with the reactant olefin like a U.S. Pat. No. 3,635,718 number publication, N-methylol compound given in a U.S. Pat. No. 2,732,316 number, and the isocyanate like a U.S. Pat. No. 3,103,437 publication A U.S. Pat. No. 3,017,280 number and the aziridine compounds like this No. 2,983,611 publication The carbodiimide system compounds like a U.S. Pat. No. 3,100,704 number publication The epoxy compound like a U.S. Pat. No. 3,091,537 number publication, and the halogen carboxyl aldehydes like mucochloric acid inorganic cross linking agents, such as organic cross linking agents, such as a dioxane derivative like dihydroxy dioxane, chromium alum, potash alum, a sulfuric-acid zirconium, and a way acid, etc. — it is — these — one sort — or two or more sorts can be combined and it can use.

[0077] As an approach of forming the acceptance layer of this invention, the coating approaches usually used, such as the size press method, the roll coater method, the blade coating-machine method, the air knife coating-machine method, the gate roll coater method, the rod bar coating-machine method, the curtain method, the slide hopper method, and the extrusion method, are used.

[0078] In the acceptance layer of this invention, various additives with still better known fixing agent of an inorganic pigment besides a binder and a hardening agent, a coloring color, a color pigment, and an ink color, ultraviolet ray absorbent, anti-oxidant, dispersant of a pigment, defoaming agent, leveling agent, antiseptics, fluorescent brightener, viscosity stabilizer, pH regulator, etc. can also be added.

[0079] It is desirable to add a surfactant in the range which does not spoil ink absorptivity in order to raise image quality in the acceptance layer of this invention. The surface active agent used may use together the thing of the class from which a type is sufficient as both an anion system a cation system the Nonion system and a betaine system, and a low-molecular thing or the thing of a macromolecule also differs. It is the surfactant of a fluorine system preferably in these.

[0080] The above-mentioned fluorochemical surfactant For example, a U.S. Pat. No. 2,559,751 number, Said 2,567,011 numbers, said 2,732,398 numbers, said 2,764,602 numbers, Said 2,806,866 numbers, said 2,809,998 numbers, said 2,915,376 numbers, Said 2,915,528 numbers, said 2,918,501 numbers, said 2,934,450 numbers, Said 2,937,098 numbers, said 2,957,031 numbers, said 3,472,894 numbers, Said 3,555,089 numbers, British JP,1,143,927,B, said 1,130,822 numbers, JP,45-37304,B, JP,47-9613,A, 49-134614, 50-117705, 50-117727, 50-121243, 52-41182, 51-12392, British American Institute of Chemists magazine (J. Chem.Soc.) 1950 2789 pages, These the 1957 2574 pages and, 2640 pages, American-institute-of-chemists magazine (J. Amer.Chem.Soc.) 79-volume 2549 pages (1957), It is compoundable by the approach indicated by 12 oil chemistry (J. Japan Oil ChemistsSoc.) 653 pages, organic chemistry meeting magazine (J. Org.Chem.) 30-volume 3524 pages (1965), etc.

[0081] It is a trade name. a certain kind among these fluorochemical surfactants of thing — Dainippon Ink & Chemicals, Inc. to megger fuck (Megafac) F — Minnesota mining – and – MANIFAKUCHUA ring company company to Fluorad (Fluorad) FC — by the trade name MONFU from an imperial chemical industry company — a roll (Monflor) — by the trade name from I eye E. I. du Pont de Nemours NEMERASU– and – company company — Zonyls (Zonyls) — a trade name — it is — moreover, FARUPEBERUKE Hoechst A.G. to RIKOBETTO (Licowet) VPF — it is marketed by the trade name, respectively.

[0082] As an amount of coating of the acceptance layer of this invention, 5 – 100 g/m<sup>2</sup> is

desirable, and is 10 – 50 g/m<sup>2</sup> more preferably. Moreover, the range of being 10–100 micrometers as thickness of an acceptance layer is 40–70 micrometers desirable especially preferably.

[0083] All over an ink absorbing layer, an organic mat agent can be used in order to raise conveyance nature.

[0084] A mat agent may be set to a photograph technical field, is known, and can be defined as being the discontinuous particle of the organic material which can be distributed in a hydrophilic organic colloid binder.

[0085] As an example of an organic mat agent, they are starch, cellulose ester (for example, cellulose acetate propionate etc.), cellulose ether, synthetic resin (for example, ethyl cellulose etc.), etc. as the example of synthetic resin — water — insoluble or a poorly soluble composition polymer — it is — for example, alkyl (meta) acrylate — Alkoxy alkyl (meta) acrylate, glycidyl (meta) acrylate, Acrylamide, vinyl ester (for example, vinyl acetate), acrylonitrile, (Meta) Independent or combination, such as an olefin, styrene (for example, ethylene etc.), and a benzoguanamine formaldehyde condensate, Or the polymer which uses combination of these, an acrylic acid, a methacrylic acid, alpha, beta-partial saturation dicarboxylic acid, hydroxyalkyl (meta) acrylate, sulfoalkyl (meta) acrylate, a styrene sulfonic acid, etc. as a monomer component can be used.

[0086] In addition, an epoxy resin, nylon, a polycarbonate, phenol resin, a polyvinyl carbazole, a polyvinylidene chloride, etc. can be used.

[0087] 3–20 micrometers has [ these mat agent ] the viewpoint of conveyance nature to a desirable weighted mean particle size, and, as for the AUW in an acceptance layer (it is attached and is also called an amount), it is desirable that it is 10 – 100 mg/m<sup>2</sup>, and it is desirable to eliminate beforehand a particle 3 micrometers [ or less ] and a particle 20 micrometers or more by the classification from the point of coating liquid ammonia quality. Moreover, these mat agent can also be used together.

[0088] The record form for ink jet printers concerning this invention means not only paper but all the so-called ink jet record material, record material puts the thing which carried out coating on the base material or which was made to contain, and things, such as a front face of the shape of a sheet and not only tabular but a can, etc. can be especially used without a limit as a base material. Moreover, also with a transparent base material, also with an opaque base material, it can respond in activity eye and can use.

[0089] As a transparent base material, each well-known thing can use it conventionally, for example, there are a film thru/or a sheet, or glass plates, such as polyester resin, cellulose acetate resin, acrylic resin, polycarbonate resin, polyvinyl chloride resin, polyimide resin, cellophane, and celluloid, etc. The viewpoint of the rigidity of a base material and transparency to polyester resin, especially a polyethylene terephthalate film are desirable in these.

[0090] As an opaque base material, these complex, such as films, such as coated paper, such as non-coated paper, such as paper of fine quality, a report grade paper, super can lender processing paper, a \*\*\*\* stencil, and tracing paper, art paper, coat paper, a light weight coat paper, fine coated paper, and a cast-coated paper, a plastic film, an opaque film containing a pigment, and a foaming film, resin coat paper, an impregnated paper, a nonwoven fabric, cloth, a metal film, and a metal plate, can be used.

[0091] In these, the resin coat paper from a viewpoint of glossiness and smooth nature and various films are desirable, and the film of a polyester system is more desirable in polyolefin resin coat paper and various films in resin coat paper from a feeling of a feel, and a high-class feeling.

[0092] Although the paper which especially a limit does not have the stencil which constitutes the resin coat paper used preferably, and is generally used can be used, a smooth stencil which is used for the base material for photographs more preferably is desirable. as the pulp which constitutes a stencil — natural pulp, playback pulp, a synthetic pulp, etc. — one sort — or two or more sorts are mixed and it is used. Additives, such as the sizing compound generally used of paper making, a paper reinforcing agent, a loading material, an antistatic agent, a fluorescent brightener, and a color, are blended with this stencil.

[0093] Furthermore, a surface sizing compound, a surface paper durability agent, the fluorescent brightener, the antistatic agent, the color, the anchoring agent, etc. may be applied to the front face.

[0094] Moreover, although there is especially no limit about the thickness of a stencil, the good thing of the surface smooth nature which impressed paper under paper milling or in the calender after paper milling, and compressed the pressure is desirable.

[0095] As resin of resin coat paper, the resin hardened with polyolefin resin or an electron ray can be used. As polyolefin resin, it is the copolymers which consist or more of two of olefins, such as a homopolymer of olefins, such as low density polyethylene, high density polyethylene, polypropylene, polybutene, and the poly pentene, or ethylene propylene rubber, and such mixture, and the thing of various kinds of consistencies and various kinds of melt viscosity characteristics (melt index) can be used for independent or them, mixing.

[0096] In the resin of resin coat paper, moreover, white pigments, such as titanium oxide, a zinc oxide, talc, and a calcium carbonate, Fatty-acid amides, such as octadecanamide and an arachidic acid amide, zinc stearate, Fatty-acid metal salts, such as calcium stearate, aluminum stearate, and magnesium stearate, Antioxidants, such as IRUGA NOx 1010 and IRUGA NOx 1076, Blue pigments and colors, such as cobalt blue, ultramarine blue, sicilian blue, and a copper phthalocyanine blue, It is desirable to add combining suitably various kinds of additives, such as a pigment of Magentas, such as cobalt violet, fast violet, and manganese purple, a color, a fluorescent brightener, and an ultraviolet ray absorbent.

[0097] The base material used by this invention is JIS. Since the thing of continuation conveyance nature of 1 – 15 g-cm improves to the environmental variation of temperature and humidity, the Taber stiffness by P-8125 is used especially preferably.

[0098] The ink jet record approach of this invention is the recording device outputted using different ink beyond \*\*5 sort. recording on the record material of this invention, and \*\* — to at least one sort of criteria colors with the recording device recorded in two or more sorts of different ink Recording on the record material of this invention or the \*\* aforementioned criteria color is characterized by what is recorded with the recording device recorded in two or more sorts of ink in which the absorbances of the ink of this criteria color differ substantially.

[0099] The ink jet record approach that the ink jet record approach used for this invention records water on the record sheet for ink jets of this invention in the ink contained 40% of the weight or more is used preferably, and the following coloring agent, a solvent object, and the ink jet record liquid that consists of other additives are used for this ink. As a coloring agent, water soluble dye, such as direct dye, acid dye, basic dye, reactive dye, or a food dye, is mentioned.

[0100] As a solvent of the ink used for the acceptance layer of this invention Water and water-soluble, various organic solvents, for example, methyl alcohol, ethyl alcohol, Propyl alcohol, isopropyl alcohol, butyl alcohol, Alkyl alcohols of the carbon numbers 1-4 of sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, etc.; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, alkylene groups, such as a diethylene glycol, — 2-6 alkylene glycol; — a glycerol — Ethylene glycol methyl ether, the diethylene-glycol methyl (or ethyl) ether, Pyrrolidones, such as pyrrolidinone, such as low-grade alkyl ether of polyhydric alcohol, such as triethylene glycol and the monomethyl ether, and 2H-pyrrolidinone, a 1-methyl-2-pyrrolidone, and 2-pyrrolidone, are mentioned. Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, the triethylene glycol monomethyl ether, and the triethylene glycol monoethyl ether, and pyrrolidones are desirable.

[0101] Although it is desirable to use the mixed solvent of water and said organic solvent from a viewpoint of clogging prevention of an ink head nozzle as for the solvent of ink, at this time, the content to the ink of water is 40 % of the weight or more, and is 50 – 90 % of the weight preferably.

[0102] As an additive to other ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0103] Moreover, in this invention, if it records with the recording device which used shade ink, the effectiveness of this invention will show up notably. For example, although the conventional color

recording device has the approach in use of using one kind each of ink to four criteria colors, Y, M, C, and K, when two or more sorts of ink is used about a certain criteria color, it can improve the formation of many gradation, and the feeling of a rough deposit of the low concentration section. especially a certain criteria color (for example, Y, M, C, K) is using the ink (shade ink) in which two or more kinds of absorbances' differ, the low concentration section reduces a feeling of a rough deposit mainly using light-colored (an absorbance — low) ink, and the high concentration section mainly uses the ink of a dark color (an absorbance — high), and a configuration out of which sufficient maximum concentration comes is known. Light color ink and dark color ink may be using the same color, and even if it is using a different color, the combination of the color from which plurality differs is also available. as the recording device which is using shade ink about such a criteria color — PM-700 — C (Seiko Epson), Picty300 (NEC), and Photo It is marketed by the trade name of Smart (Hewlett Packard), and it is the description to output in a total of six sorts of ink of the ink of light-colored M and light-colored C other than Y, M, C, and K. Moreover, BJC-700J (canon company make) are mentioned as an example of the recording device of the same method.

[0104]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these.

[0105] The base material which carried out 20 g/m<sup>2</sup> coating of the resin constituent which becomes the front face of the base material of <production of base material> basis weight 60 g/m<sup>2</sup> from the low-density-polyethylene 70 section and the high-density-polyethylene 20 section, and carried out 20g[m ] 2 coating of the resin constituent which becomes a rear face from the low-density-polyethylene 50 section was produced.

[0106] The 4 opening flask which is 300ml of composition of colloidal silica by which <composition (1) of non-subtlety particle (polymer joint inorganic particle) which organic cationic polymer combined> surface treatment was carried out was equipped with the agitator, and 100g (the content of a silica is 20%) was supplied for colloidal silica (the trade name Snow tex OUP, the Nissan chemistry company make). 3-methacryloxy propyl trimethoxysilane was dropped at this, stirring 1.0g and 10g of distilled water. It was made to react at a room temperature furthermore for 30 minutes, and the target colloidal silica by which surface treatment was carried out was obtained as a distributed object.

[0107] (2) The 4 opening flask of 2l. of composition of an intermediate-product particle was equipped with an agitator, a thermometer, gas installation tubing, and a capacitor, 200g and a surfactant (trade name TORAKKUSU H-45) were thrown in for distilled water, and 7.7g and a potassium hydroxide were thrown in for 0.78g. Nitrogen gas was stirred for 30 minutes at the room temperature with the sink, and was deaerated. 12.1g and a divinylbenzene were supplied for styrene, 12.9g was supplied for 0.8g and dimethylamino methyl styrene to this, and 13.7g of dispersion liquid of the colloidal silica which carried out surface treatment by the above (1) further was added. It heated until inside \*\* became 70 degrees C, stirring by per minute 300 revolution, and 0.84g (iso cyano valeric acid) of 2 and 2'-azobis was added after that. The polymerization of the heating stirring was then performed and carried out under the nitrogen air current for 5 hours.

[0108] After reaction termination, after removing unnecessary solid content using a glass filter, the intermediate-field particle made into the object was obtained as an opaque white chromatism object.

[0109] (3) The 4 opening flask of 300ml of composition of a polymer joint inorganic particle (1) was equipped with the agitator, and 100g of intermediate-field particles compounded above (2) was supplied. It was dropped stirring to this having acetonitrile 30 bet it for 30 minutes. Furthermore 3.1g of benzyl chlorides was dropped, and heating stirring was carried out in the 60-degree C oil bath for 6 hours. After reaction termination, after cooling radiationally to a room temperature, about 40ml of bottom solvents of reduced pressure was distilled out. Distilled water was added to the remaining liquid and the polymer joint inorganic particle (1) which adjusts the whole to 100g and is made into the object was obtained as an opaque white chromatism object.

[0110] (4) While using as the compound of table 1 publication the non-subtlety particle by which surface treatment is carried out, the ratio of each monomer was made into the value of a



publication among an instantiation compound, and also it is an instantiation compound (2) by the same actuation, The polymer joint inorganic particle (1) which has (3), (4), (7), (8), and (10) in a mother nucleus, (2), (3), (4), (7), (8), and (10) were compounded.

[0111] The polymer joint inorganic particle created by the example 1 – the 13 above-mentioned approach (1), The coating liquid which carried out 12 weight sections addition of the polyvinyl alcohol polymerization degree 2500 (PVA may only be called below) for (2), (3), (4), (7), (8), and (10) 98% whenever [ 88 weight sections and saponification ] was created, coating was carried out so that desiccation solid content might be set to 20g/m<sup>2</sup> with a wire bar, and the sample was created.

[0112] The coating liquid which carried out 12 weight sections addition of the polyvinyl alcohol degree of polymerization 2500 for one to example of comparison 3 colloidal silica, alumina sol, and a zinc oxide 98% whenever [ 88 weight sections and saponification ], respectively was created, coating was carried out so that desiccation solid content might be set to 20g/m<sup>2</sup> with a wire bar, and the sample was created.

[0113] Example of comparison 4 polymerjournal, vol.21, No.6, p475 (1989), and Journal of The non-subtlety particle which graft-ized acrylate by using a silica as a nucleus polymerscience, A, vol.29, p697 (1992), a front face, vol.30, No.1, p74 (1992), etc. according to the approach of a publication was created. Then, the coating liquid which carried out 12 weight sections addition of the polyvinyl alcohol degree of polymerization 2500 for the created non-subtlety particle 98% whenever [ 88 weight sections and saponification ] was created, coating was carried out so that desiccation solid content might be set to 20g/m<sup>2</sup> with a wire bar, and the sample was created.

[0114] Next, the following approaches estimated the sample created in the above-mentioned examples 1–13 and the examples 1–4 of a comparison. At this time, all assessment was outputted using Seiko Epson ink jet printer PM700C. Moreover, as an output environment at this time, it carried out in 25 degrees C and the environment of 70%RH except for generating of a crack supposing the rainy season term.

[0115] The sample <generating of a crack> Obtained was judged to 210mmx297mm(A4), ten samples with a bore of 30mm stopped on the tape were produced [ it rounded off to the longitudinal direction so that it might become cylindrical, and ], and it was left for one week by 15 degrees C and 20% environment. then, 5 or 6 random per sheet — the 10mmx10mm range — determining — the number of a crack — an optical microscope — measuring — A4 — the number of average cracks was made into the number of cracks per sheet.

[0116] <Bleeding> SCID N3 image was printed and the lap of the dot of cyanogen-Magenta and Magenta-yellow and yellow-cyanogen was observed with the optical microscope.

O; most color muddiness was not observed but the image also with high sharp nature was obtained.

O; an image is satisfactory level although color muddiness of some arises only into a cyanogen-Magenta part.

\*\*; color muddiness is in a cyanogen-Magenta and Magenta-yellow part, and the red part of an image can be seen in the shape of nonuniformity.

x; color muddiness has arisen in the total color and it became the image which faded on the whole.

[0117] <Beading> yellow, a Magenta, cyanogen, black, Green, blue, and the maximum-density section of red were outputted, and viewing estimated the rough deposit degree.

O; there is no rough deposit in each color, and excel in it.

O; although few rough deposits are checked by the Green section, it is not actual harm level.

\*\*; a rough deposit is checked by the Green section and the blue section.

x; on the whole, a rough deposit is severe and is not set to goods level.

[0118] After having outputted the natural image of <drying> A4 size, having rounded off so that it might become the bore of 4cm about a form after 10 minutes, and stopping on a tape, the sample was observed one day after and viewing estimated the imprint degree on the back.

[0119] O; completely with no imprint.

O; with [ although there is an imprint slightly ] no practical skill top problem.

\*\*; an imprint occurs in the high concentration section.

x; an imprint occurs and the film peels from an imprint side.

[0120]

[A table 1]

	有機がむ性シリカ 無機微粒子	有機がむ性シリカに結合した無機微粒子 有機がむ性シリカ 例示化合物(1)	有機がむ性シリカ 無機微粒子比 0.5/99.5	受容層中の 含有率(重量%) 88	フッ素シリカ	ヒートシリカ	乾燥性	クラックの発生 (個/44サイズ)
実施例 1	シリカ *1	例示化合物(1)	0.5/99.5	88	○	○	○	2
実施例 2	シリカ *1	例示化合物(2)	0.5/99.5	88	○	○	○	1
実施例 3	シリカ *1	例示化合物(3)	0.5/99.5	88	○	○	○	2
実施例 4	シリカ *1	例示化合物(4)	0.5/99.5	88	○	○	○	1
実施例 5	シリカ *1	例示化合物(7)	0.5/99.5	88	○	○	○	1
実施例 6	シリカ *1	例示化合物(8)	0.5/99.5	88	○	○	○	1
実施例 7	シリカ *1	例示化合物(10)	0.5/99.5	88	○	○	○	2
実施例 8	酸化シリカ	例示化合物(3)	0.5/99.5	88	○	○	○	5
実施例 9	シリカ	例示化合物(3)	0.5/99.5	88	○	○	○	4
実施例 10	酸化シリカ	例示化合物(3)	0.5/99.5	88	○	○	○	7
実施例 11	酸化シリカ	例示化合物(3)	0.5/99.5	88	○	○	○	7
実施例 12	非晶質シリカ *9	例示化合物(3)	0.5/99.5	88	○	○	○	1
実施例 13	酸化シリカ *2	例示化合物(3)	0.5/99.5	88	○	○	○	8
比較例 1	シリカ *2	未結合	0.5/99.5	88	△	△	△	21
比較例 2	酸化シリカ	未結合	0.5/99.5	88	△	△	△	33
比較例 3	シリカ	未結合	0.5/99.5	88	△	△	△	20
比較例 4	シリカ	シリカ *1	0.5/99.5	88	○	△	△	35

コロイダルシリカ \*1 日産化学社製スノーテックス OUP

コロイダルシリカ \*2 日産化学社製スノーテックス O

非晶質シリカ \*3 日本 AEROSIL 社製 AEROSIL 200

As shown also in a table 1, the record form for ink jet printers of this invention prevents generating of a crack, and under a high-humidity condition, drying can be raised, and a high definition image can be obtained by high concentration, and it also turns out that a good result is shown.

[0121] Using the colloidal silica (the Nissan chemistry company make; Snow tex OUP) and the instantiation compound 3 which were used in the 14 to example 29 example 3, adjust an organic cationic polymer / non-subtlety particle ratio so that it may become the value of table 2 publication, and adjust the amount of the polymer joint inorganic particle in coating liquid, and the

content in an acceptance layer was made to become the value of table 2 publication, and also it is the same actuation. It evaluated by creating a sample. The following assessment was added at this time.

[0122] After performing the same assessment as generating of a <mustache-like myogenesis> crack, the alphabet (26 characters) surplus was printed all over the sample, and the muscle of the shape of a mustache generated on a character boundary line was observed visually.

O; generating of a mustache-like muscle was not seen at all.

O; less than five generating is level which is satisfactory at all on practical skill, although it saw.

Level which generating of \*\*:5-30 place is checked and is a little conspicuous.

Generating beyond x;30 place is checked and it is problematic level on practical skill.

[0123] <Glossiness after printing> yellow, a Magenta, cyanogen, black, Green, blue, and the maximum-density section of red were outputted, and after getting dry enough, glossiness was checked visually.

O; each color is maintaining glossiness.

O; the other colors of a falling [ the glossiness of the black section ]—a little thing are maintaining glossiness, and are level which is satisfactory at all on practical skill.

\*\*; although it is the level in which glossiness is inferior a little on the whole, and concentration is also a little inferior, actual harm nature has no problem.

x; there is no glossiness in each color and it is problem level.

[0124]

[A table 2]



quickly in recent years, or the roll printer, drying degradation, and generating of the muscle of the shape of a mustache produced on generating of a crack, or the boundary of the printing section and the non-printed section.

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[Translation done.]

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## PRIOR ART

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[Description of the Prior Art] Ink jet recording apparatus (in this description, it is also called an ink jet printer.) However, of course, this invention is applicable to the recording device at large which is not limited to the so-called printer. There is little noise, and since it is also easy to perform multicolor record by using two or more ink nozzles possible [ high-speed printing ], it has spread quickly as an image information output unit for computers especially in recent years.

[0003] Moreover, there are some ink jet printers which were developed for full color record and which can output an image [ high definition like it is equal to the color picture of a film photo method ]. Moreover, the content of the image to output is also expanded to a color block copy, a design image, etc. as which the image quality near a photograph is required from an alphabetic character, a graphic form, etc.

[0004] therefore, as the record medium, it rubs from the coat paper and the regular paper of glossiness or concentration which become low — carry out — the glossy paper or the gloss film using the resin coat paper out of which the opaque film which has the glossiness more near a photograph, and gloss come — or many cast-coated papers which carried out the cast of the front face of coat paper, and gave specular-gloss nature have come to be used.

[0005] It corresponds to these and using the water-soluble polymer which swells or dissolves water color ink as an ink absorbing layer (or coat layer) is proposed. For example, in JP,62-263084,A, the acceptance layer in which a mean molecular weight contains [ the record sheet for ink jet printers which it dries by the cold dry cleaning method once the acceptance layer formed from the gelatin water solution of Specification pH makes the gel state the gelatin applied in JP,6-64306,A, and is obtained ] 5x10<sup>4</sup> or more polyethylene oxide by JP,62-214985,A is proposed, respectively.

[0006] Moreover, by one side, the acceptance layer of the porosity mold using a non-subtlety particle is proposed. The acceptance layer of a porosity mold prepares a detailed opening by the particle, and receives ink, and drying is dramatically excellent and has the advantage that there is also little color muddiness and it can output the image of high resolution.

[0007] It cannot respond with the advent of a high speed and a multi-discharge quantity ink jet printer, but color muddiness (bleeding) and beading (Pacific cod) produce a print rate and ink absorption capacity between dots, and it is becoming impossible however, to obtain a quality image in recent years. Furthermore, since these printers have realized many gradation by using shade ink, the amount of ink increases, by the high-humidity condition, poor desiccation especially occurs frequently, and they are posing a serious problem. Although there is the approach of thickening thickness of an acceptance layer as a means to increase absorption capacity in order to solve these problems, poor conveyance arises conversely, or it leads to a cost rise, and is not desirable. Furthermore, since the porosity mold acceptance layer used the non-subtlety particle, the film reinforcement of the acceptance layer itself was high, and it turned out that it also has the trouble of being easy to produce a crack (crack) since distraction nature is low.

[0008] These troubles pose a still bigger problem, when applying as an object for roll printers. For example, although there is a service bureau which creates a poster etc. as a field which uses a roll printer, since increasing the amount of ink and usually using it with the color-balance adjustment means called RIP in order to improve the sharp nature and contrast of an alphabetic character is

generally used, what it is further easy to generate from the desktop mold printer by which an amateur user uses the above problems is the actual condition. Since it is twisted to the shape of a roll strongly also as a product gestalt, it is easy to be generated, and if a crack is printed by the part, the problem on which outflow and image quality deteriorate [ ink ] in the shape of a mustache along with a crack will produce it. Moreover, since it rounds off and is kept after printing for a long period of time, if drying deteriorates, since most users will imprint at the rear face, they have a possibility of spoiling quality. The actual condition is being unable to use him, if a pro user's is most and the user who uses a roll printer does not solve these problems.

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[Translation done.]

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] Record material, such as a record sheet for ink jet printers by this invention, solves degradation (beading, bleeding, etc.) of the image quality produced by the high speed and multi-discharge quantity printer which were mentioned above, and which are increasing quickly in recent years, or the roll printer, drying degradation, and generating of the muscle of the shape of a mustache produced on generating of a crack, or the boundary of the printing section and the non-printed section.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The object of this invention is to offer the record form for ink jet printers and the record approach of solving degradation (beading, bleeding, etc.) of the image quality produced by the high speed and multi-discharge quantity printer which were mentioned above, and which are increasing quickly in recent years, or the roll printer, drying degradation, and generating of the muscle of the shape of a mustache produced on generating of a crack, or the boundary of the printing section and the non-printed section.

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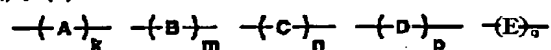
**MEANS**

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[Means for Solving the Problem] The above-mentioned technical problem of this invention is the record form for ink jet printers characterized by containing the non-subtlety particle which the organic cationic polymer combined in 1. acceptance layer, and the record form for ink jet printers of said one publication characterized by 2. aforementioned organic cationic polymer consisting of compounds expressed with the following general formula (I), [0011]

[Formula 3]

一般式 (I)

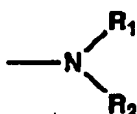


[0012] In a general formula (I), (A) expresses the monomeric unit which carried out the polymerization of the monomer which has quaternary ammonium, and which can be copolymerized, and (B) expresses the monomeric unit which carried out the polymerization of the monomer which is contained at least one of the structures expressed with the following general formula (II), (III), (IV), and (V), and which can be copolymerized.

[0013]

[Formula 4]

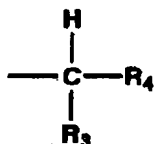
一般式 (II)



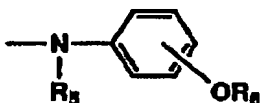
一般式 (III)



一般式 (IV)



一般式 (V)



[0014] In a general formula (II), R1 and R2 express an aliphatic series radical, and Z expresses a nonmetal atom group required to form 5 members or a six membered ring in collaboration with -C-N=C- in a general formula (III). In a general formula (IV), R3 and R4 express an aromatic series radical, a halogen atom, a cyano group, and an oxy-carbonyl group. In a general formula (V), R5 expresses a hydrogen atom and an aliphatic series radical, and R6 expresses an aliphatic series radical.

[0015] In the above-mentioned general formula (I), (C) expresses the monomeric unit which carried out the polymerization of the monomer which has at least two ethylene-like unsaturated bond radicals, and which can be copolymerized, and (D) expresses the monomeric unit which carried out the polymerization of (A), (B), and the monomer in which the copolymerization of those other than (C) is possible.

[0016] In the above-mentioned general formula (I), the monomeric unit expressed with (E) expresses the monomeric unit which has the radical which can form said non-subtlety particle and covalent bond.

[0017] Ten to 95-mol%, in m, zero to ten-mol%, p expresses zero to 80-mol %, and, as for q, n expresses [ k ] 0.1 to 20-mol % zero to 30-mol%. However, the sum total of k, m, n, p, and q is 100-mol %.

[0018] 3. Record Form for Ink Jet Printers of Said 1 or 2 Publications to which Organic Cationic Polymer Weight Ratio (Organic Cationic Polymer / Non-Subtlety Particle) to Said Non-Subtlety Particle is Characterized by or More 1/99 being 99/1 or Less, 4. The record form for ink jet printers given in either [ to which the non-subtlety particle which said organic cationic polymer combined is characterized by containing ten to 99% of the weight in an acceptance layer / said ] 1-3, 5. with the recording device outputted to said any of 1-4 which are characterized by a base material being polyolefine coat paper using the record form for ink jet printers of a publication, and 6.5 or more sorts of different ink the color ink jet record approach characterized by what is

recorded on a record form given in either [ said ] 1-5, and 7. — to at least one sort of criteria colors with the recording device recorded in two or more sorts of different ink The color ink jet record approach characterized by what is recorded on a record form given in either [ said ] 1-5, 8. Said criteria color is attained by each of color ink jet record approach \*\* of said seven publications characterized by what is recorded with the recording apparatus recorded in two or more sorts of ink in which the absorbances of the ink of this criteria color differ substantially.

[0019]

[Embodiment of the Invention] This invention is further explained to a detail. The non-subtlety particle which the organic cationic polymer first used for this invention combined is explained.

[0020] The non-subtlety particle used for this invention is a particle which has a detailed particle size, for example, a kaolin (clay), talc, titanium oxide, a zinc oxide, a zirconium dioxide, cerium oxide, an oxidization yttrium, the tin oxide, an antimony oxide sol, a niobium oxide sol, an aluminum silicate, an aluminum hydroxide, an aluminum oxide, a calcium silicate, a magnesium silicate, colloidal silica, or amorphous silica is mentioned.

[0021] An aluminum oxide, colloidal silica, amorphous silica, a zinc oxide, and titanium oxide are especially mentioned preferably in these. Although there is especially no limit in the configuration of these inorganic particle, the shape of a globular form, a cube form, a cylinder, a needle, and a chain, annular, plate-like, etc. are mentioned preferably. As mean particle diameter, the range of 1-500nm is desirable.

[0022] These non-subtlety particles are combined by the organic cationic polymer described below, it is or more 10/90 or less 90/10 range that it is or more 1/99 99/1 or less range desirable still more preferably, and the weight ratio (an organic cationic polymer / non-subtlety particle) of an organic cationic polymer to a non-subtlety particle is or more 20/80 80/20 or less range especially preferably.

[0023] The non-subtlety particle which the organic cationic polymer combined in this invention is in the condition that the reaction radical which can be connected with a non-subtlety particle in an organic cationic polymer means the thing in the condition of being selectively combined with the non-subtlety particle, and is covered preferably (these particles may be called a polymer joint inorganic particle below).

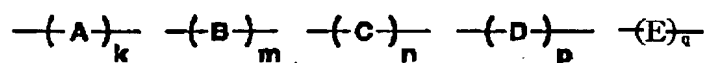
[0024] Next, the organic cationic polymer used in this invention is explained.

[0025] The organic cationic polymer used in this invention has the unit expressed with the following desirable general formulas (I).

[0026]

[Formula 5]

一般式 (I)

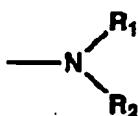


[0027] In a general formula (I), (A) expresses the monomeric unit which carried out the polymerization of the monomer which has quaternary ammonium, and which can be copolymerized, and (B) expresses the monomeric unit which carried out the polymerization of the monomer which is contained at least one of the structures expressed with a general formula (II), (III), (IV), and (V), and which can be copolymerized.

[0028]

[Formula 6]

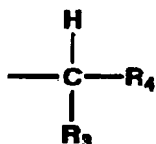
一般式 (II)



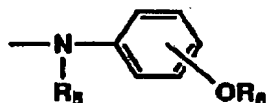
一般式 (III)



一般式 (IV)



一般式 (V)



[0029] In a general formula (II), R1 and R2 express an aliphatic series radical, and Z expresses a nonmetal atom group required to form 5 members or a six membered ring in collaboration with  $-C=N=C-$  in a general formula (III). In a general formula (IV), R3 and R4 express an aromatic series radical, a halogen atom, a cyano group, and an oxy-carbonyl group. In a general formula (V), R5 expresses a hydrogen atom and an aliphatic series radical, and R6 expresses an aliphatic series radical.

[0030] In the above-mentioned general formula (I), (C) expresses the monomeric unit which carried out the polymerization of the monomer which has at least two ethylene-like unsaturated bond radicals, and which can be copolymerized, and (D) expresses the monomeric unit which carried out the polymerization of (A), (B), and the monomer in which the copolymerization of those other than (C) is possible.

[0031] In the above-mentioned general formula (I), the monomeric unit expressed with (E) expresses the monomeric unit which has the non-subtlety particle used for this invention, and the radical which can form covalent bond.

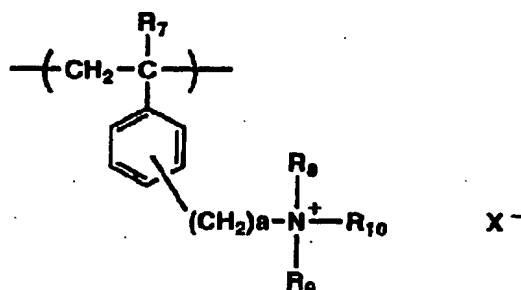
[0032] Ten to 95-mol%, in m, zero to ten-mol%, p expresses zero to 80-mol %, and, as for q, n expresses [ k ] 0.1 to 20-mol % zero to 30-mol%.

[0033] In the above-mentioned general formula (I), the monomeric unit of (A) expressed with the following general formulas (VI), (VII), and (VIII) (IX) is desirable.

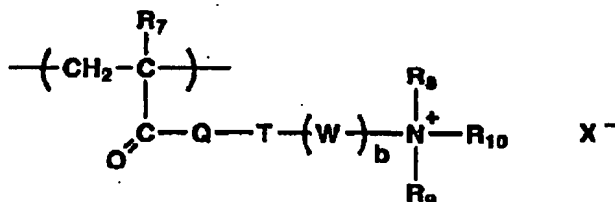
[0034]

[Formula 7]

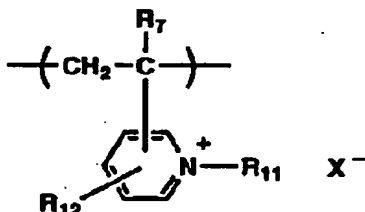
一般式 (VI)



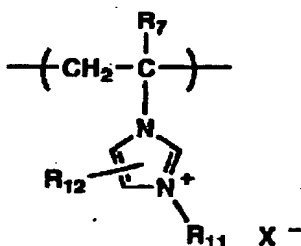
一般式 (VII)



一般式 (VIII)



一般式 (IX)



[0035] In the above-mentioned general formula (VI), (VII), and (VIII) (IX), R7 expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R7, a hydrogen atom or a methyl group is desirable.

[0036] In the above-mentioned general formula (VI), (VII), and (VIII) (IX), R8, R9, R10, and R11 express the aliphatic series radical (they are a KISHIRU radical, benzyl, etc. to a methyl group, an ethyl group, and cyclo) of the carbon atomic numbers 1-10. Even if mutually the same, you may differ, and it may join together mutually, and the substituent expressed with these [ R8, R9 and R10 ] may form cyclic structure. It is a methyl group, an ethyl group, and benzyl preferably as R8, R9, and R10, and a methyl group and especially benzyl are desirable.

[0037] In the above-mentioned general formula (VI), (VII), and (VIII) (IX), X expresses an anion, for example, halogen ion (for example, a chloride ion, bromine ion, iodine ion, etc.), alkyl-sulfuric-acid ion (for example, methylsulfuric acid ion etc.), alkyl or aryl sulfonic-acid ion (for example, methansulfonic acid ion, p-toluenesulfonic-acid ion, etc.), acetic-acid ion, etc. are mentioned. Among these, halogen ion and especially alkyl-sulfuric-acid ion are desirable.

[0038] In the above-mentioned general formula (VI), a expresses the integer of 1 to 4.

[0039] In the above-mentioned general formula (VII), Q expresses an oxygen atom or a nitrogen atom. T and W express the connection radical of bivalence, for example, express a xylene radical, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-, and a phenylene group to ethylene, 1, and 4-cyclo. b expresses 0 or 1.

[0040] In the above-mentioned general formula (VIII) and (IX), R12 expresses radicals, such as a

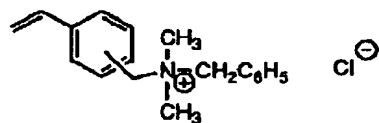
hydrogen atom, aliphatic series radicals (for example, a methyl group, t-butyl, etc.), aromatic series radicals (for example, phenyl group etc.), a halogen atom, a cyano group, acyl groups (for example, an acetyl group, benzoyl, etc.), oxy-carbonyl groups (for example, methoxycarbonyl group etc.), aminocarbonyl radicals (for example, aminocarbonyl radical etc.), and a nitro group.

[0041] In the above-mentioned general formula (I), the instantiation compound of a monomer led to the monomeric unit expressed with (A) is shown below.

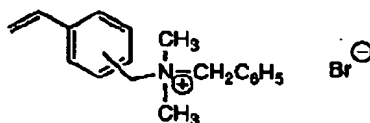
[0042]

[Formula 8]

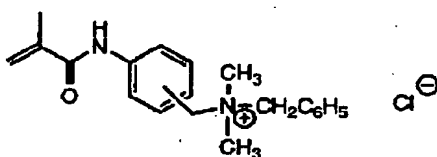
(A-1)



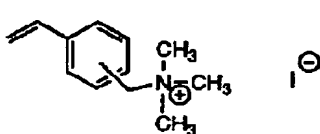
(A-2)



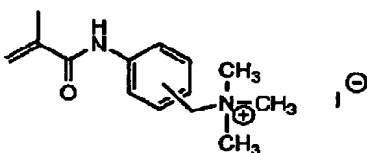
(A-3)



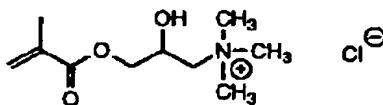
(A-4)



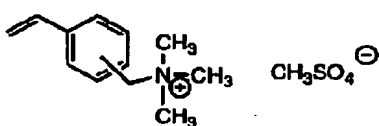
(A-5)



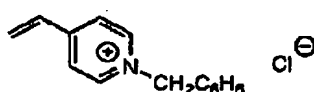
(A-6)



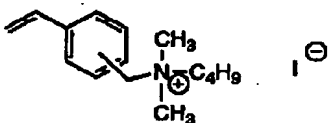
(A-7)



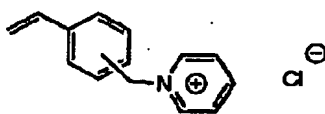
(A-8)



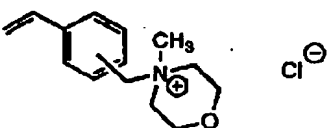
(A-9)



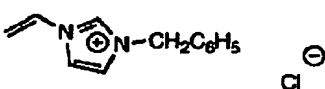
(A-10)



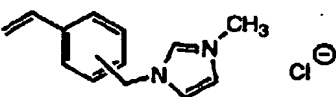
(A-11)



(A-12)



(A-13)

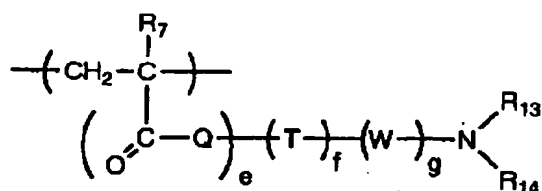


[0043] In the above-mentioned general formula (I), the following general formulas (X), (XI), and (XII) the monomeric unit of (B) expressed are desirable.

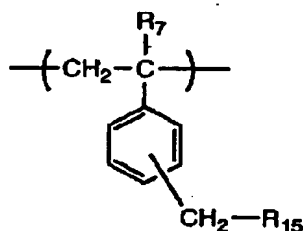
[0044]

[Formula 9]

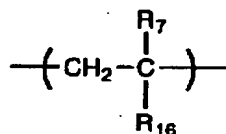
一般式 (X)



一般式 (XI)



一般式 (XII)



[0045] the above-mentioned general formula (X) and (XI) — and (XII) it sets and R7 expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R7, a hydrogen atom or a methyl group is desirable.

[0046] In the above-mentioned general formula (X), Q expresses an oxygen atom or a nitrogen atom. T and W express the connection radical of bivalence, for example, express ethylene, 1, 4-cyclo hexylene radical,  $\text{---CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O---}$ ,  $\text{---CH}_2\text{CH}(\text{OH})\text{CH}_2\text{---}$ , and a phenylene group. e, f, and g express 0 or 1, respectively (however, when e is 1, neither f nor g is 0). R13 and R14 express a hydrogen atom, an alkyl group, and an aryl group. The alkyl group and aryl group which are expressed with these [ R13 and R14 ] may join together mutually, and may form cyclic structure.

[0047] In the above-mentioned general formula (XI), R15 expresses a halogen atom (for example, chlorine atom), an aromatic series radical (for example, phenyl group), an aryloxy group (for example, phenoxy group), a hydroxy group, etc.

[0048] In the above-mentioned general formula (XII), R16 expresses 2-pyridyl radical, 4-pyridyl radical, and 1-imidazole radical.

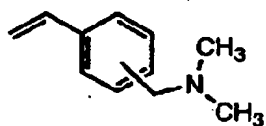
[0049] In the above-mentioned general formula (I), the instantiation compound of a monomer led to the monomeric unit expressed with (B) is shown below.

[0050]

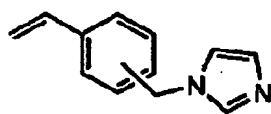
[Formula 10]



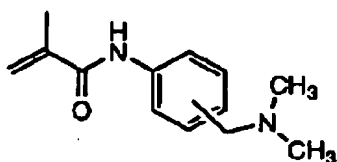
B-1



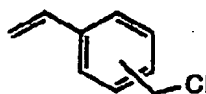
B-2



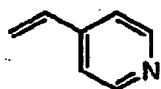
B-3



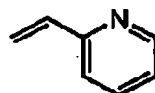
B-4



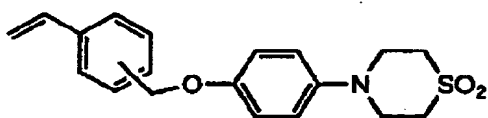
B-5



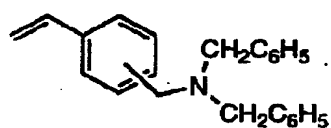
B-6



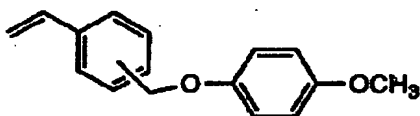
B-7



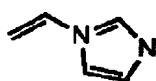
B-8



B-9



B-10



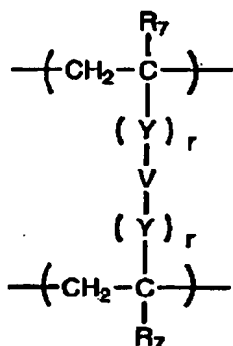
[0051] In the above-mentioned general formula (I), a divinylbenzene, ethylene glycol methacrylate, ethylene glycol acrylate, hydroquinone methacrylate, hydroquinone acrylate, an ethylene JIMETA krill amide, ECHIRENJI acrylamide, etc. are mentioned as a monomer led to the monomeric unit expressed with (C).

[0052] In the above-mentioned general formula (I), the monomeric unit of (C) expressed with the following general formulas (XIII) is desirable.

[0053]

[Formula 11]

一般式 (XIII)



[0054] In the above-mentioned general formula (XIII), R<sub>7</sub> expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R<sub>7</sub>, a hydrogen atom or a methyl group is desirable. Moreover, V expresses the connection radical of bivalence, for example, expresses arylene radicals (for example, a phenylene group, a naphthylene radical, etc.) and alkylene groups (for example, a methylene group, 1, 4-butylene radical, etc.). Y expresses an ester bond (for example, -C(=O)-O-, -O-C(=O)-), amide association (for example, -C(=O)-NH-, -NH-C(=O)-, -SO<sub>2</sub>-NH-), ether linkage (-O-), etc., and r expresses 0 or 1.

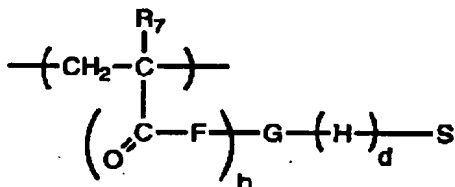
[0055] In the above-mentioned general formula (I), ethylene, a propylene, 1-butene, isobutene, styrene, alpha methyl styrene, vinyltoluene, an acrylic acid and its ester or amide derivatives (for example, a methyl acrylate, butyl acrylate, t-butyl acrylamide, etc.), a methacrylic acid and its ester or amide derivatives (for example, a methyl methacrylate, methacrylic-acid benzyl, n-butyl methacrylamide, etc.), acrylonitrile, a methacrylonitrile, etc. are mentioned as a monomeric unit expressed with (D), for example.

[0056] In the above-mentioned general formula (I), the monomeric unit of (E) expressed with the following general formulas (XIV) is desirable.

[0057]

[Formula 12]

一般式 (XIV)



[0058] In the above-mentioned general formula (XIV), R<sub>1</sub> expresses a hydrogen atom or the aliphatic series radicals (for example, a methyl group, an ethyl group, n-butyl, etc.) of the carbon atomic numbers 1-4. As R<sub>1</sub>, a hydrogen atom or a methyl group is desirable. F expresses -O- or -N(R)- (the inside R of a formula expresses a hydrogen atom, an alkyl group, or an aryl group), and b expresses 0 or 1.

[0059] In the above-mentioned general formula (XIV), G and H express the connection radical of bivalence, for example, a methylene group, ethylene, 1, 4-cyclo hexylene radical, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O-, a phenylene group, etc. are mentioned. d expresses the integer of 0, or 1-3.

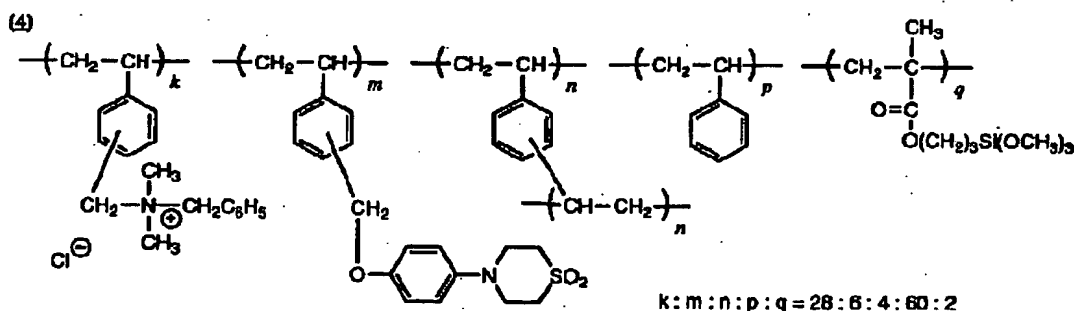
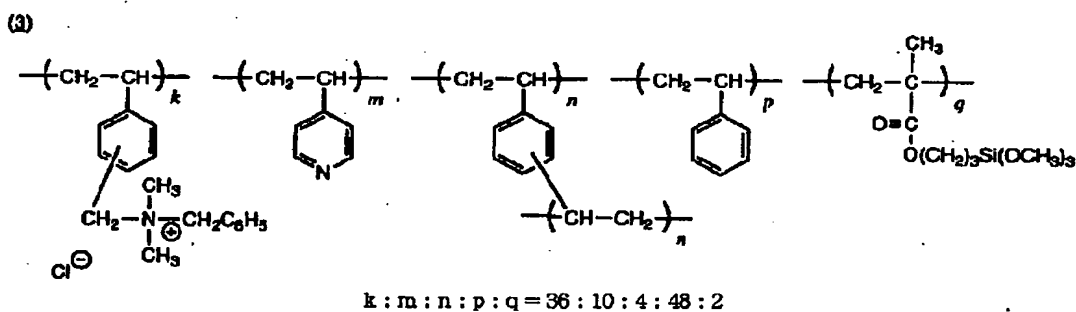
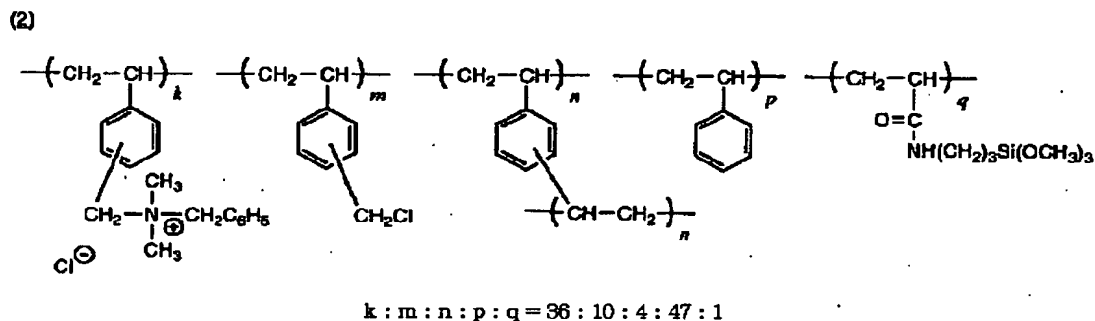
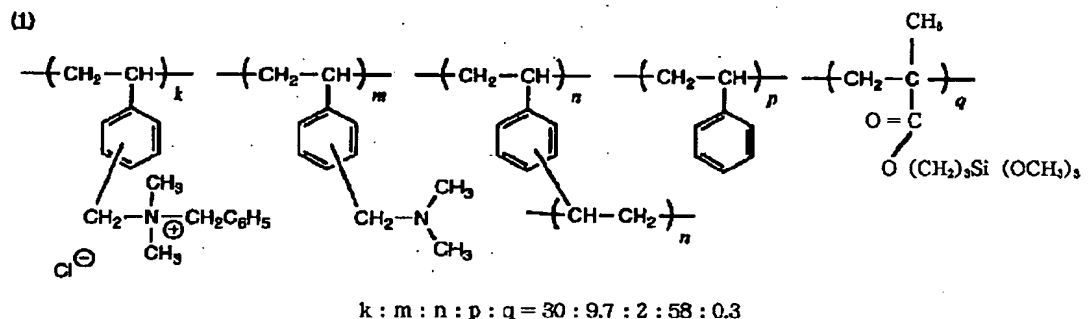
[0060] In the above-mentioned general formula (XIV), S can mention the radical which expresses the non-subtlety particle used for this invention, and the radical which can form covalent bond, for

example, is expressed with  $-\text{SiX}_3$ . (X expresses radicals, such as halogen atom (for example, chlorine atom),  $-\text{OR}$  (R expresses acyloxy radicals, such as alkoxy group [ , such as a hydrogen atom, a methoxy group, and an ethoxy radical, ], acetoxy radical, and benzyloxy radical, among formula), and  $-\text{NRR}'$  (R and R' expresses aryl groups, such as alkyl groups, such as a hydrogen atom, a methyl group, and t-butyl, and a phenyl group, among a formula), among a formula.)

Although the instantiation compound of an organic cationic polymer used in this invention is shown below, this invention is not limited to this. In addition, the illustrated polymer includes the following repeat unit at a following rate, respectively.

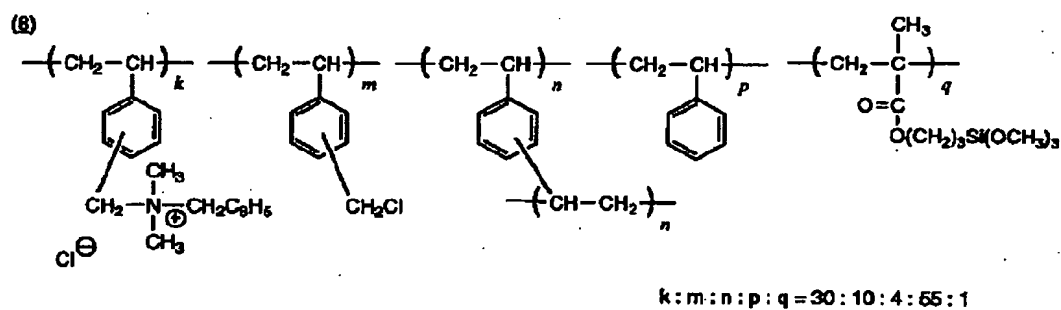
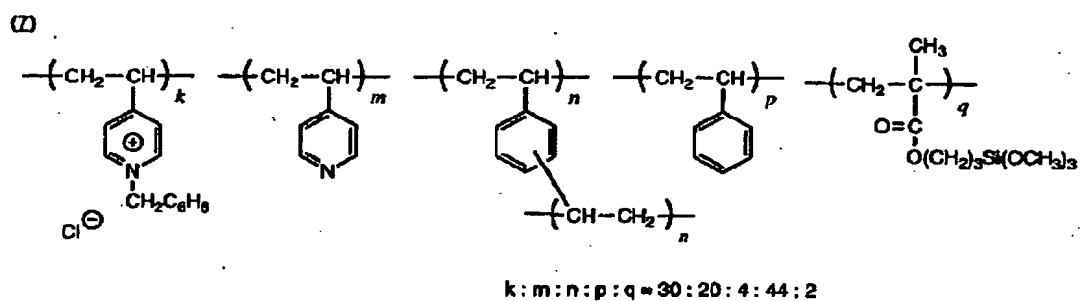
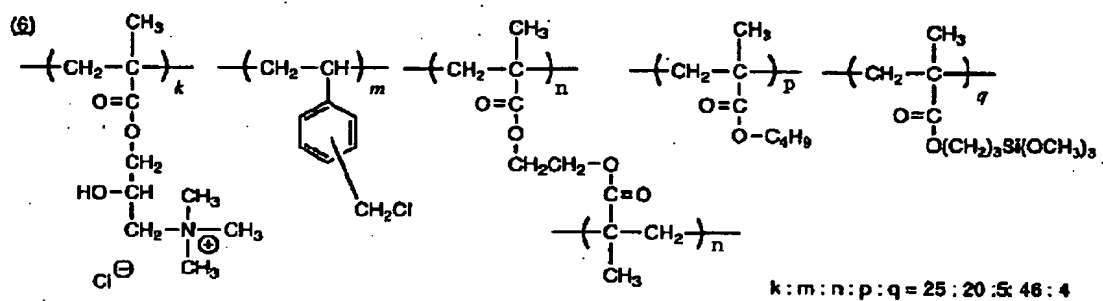
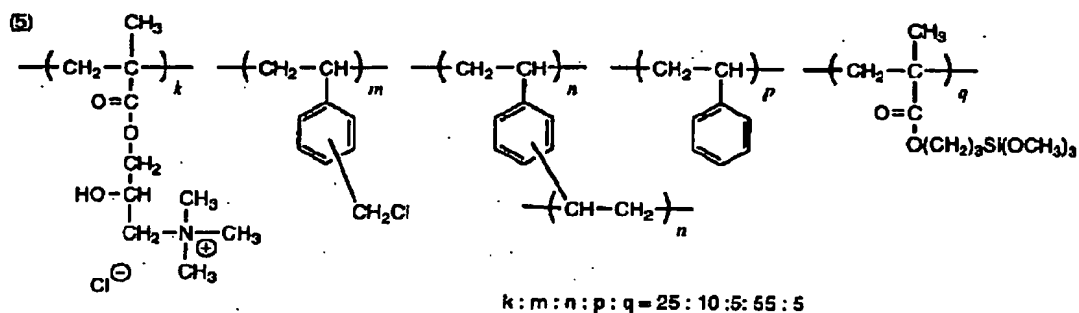
[0061]

[Formula 13]



[0062]

[Formula 14]



[0063]  
[Formula 15]



approach of combining by performing a polymerization reaction on a front face, and (5) — the approach of combining with a non-subtlety particle, since the organic polymer which introduced the coupling agent into the polymer beforehand is compounded etc. These approaches are explained to the report of for example, the Society of Fiber Science and Technology, Japan, the 49th volume, the report of a 130–136–page publication and a front face, the 28th volume, and a 285–298–page publication etc. at the detail.

[0065] next, the water-soluble binder preferably used by this invention — and — or gelatin is explained.

[0066] Although either can be used if it is gelatin which used the collagen of an animal as the raw material as gelatin preferably used for this invention, the gelatin which used as the raw material a pig skin, oxbone, and the collagen that used the cow bone as the raw material is more desirable. Although there is especially no limit as a class of gelatin, furthermore, liming gelatin, acid-treatment gelatin and derivative gelatin (for example, JP,38-4854,B —) 39-5514, 40-12237, 42-26345, A U.S. Pat. No. 2,525,753 number, said 2,594,293 numbers, said 2,614,928 numbers, said — No. 2,763,639 — said — No. 3,118,766 — said — No. 3,132,945 — said — No. 3,186,846 — said — No. 3,312,553 and British JP,861,414,B — said — the derivative gelatin of a publication can be used for No. 103,189 etc. combining independent or them. If acid-treatment gelatin is used, it is advantageous especially in respect of a water resisting property.

[0067] As an amount of coating of the gelatin contained in the acceptance layer of this invention, 3 – 20 g/m<sup>2</sup> is 5 – 15 g/m<sup>2</sup> desirable still more preferably as solid content.

[0068] As a water-soluble polymer preferably used by this invention, for example, polyvinyl alcohol vinyl formals, such as polyvinyl pyrrolidones, polyvinyl pyridinium halide, and various denaturation polyvinyl alcohol, and the derivative (JP,60-145879,A —) of those 60-220750, 61-143177, 61-235182, Refer to 61-235183, 61-237681, and 61-261089, Polyacrylamide, the poly dimethyl acrylamide, poly dimethylamino acrylate, Sodium polyacrylate, an acrylic-acid methacrylic-acid copolymer salt, polymethacrylic acid soda, the polymer (JP,60-168651,A —) containing acrylic radicals, such as an acrylic-acid vinyl alcohol copolymer salt To 62-9988 etc., a publication, starch, oxidization starch, carboxyl starch, Dialdehyde starch, cation-ized starch, a dextrin, sodium alginate, Gum arabic, casein, a pullulan, a dextran, methyl cellulose, naturally-occurring-polymers ingredients, such as ethyl cellulose, a carboxymethyl cellulose, and hydroxypropylcellulose, or the derivative (JP,59-174382,A —) of those 60-262685, 61-143177, 61-181679, To 61-193879, 61-287782, etc., a publication, a polyethylene glycol, A polypropylene glycol, polyvinyl ether, polyglycerin, A maleic-acid alkyl vinyl ether copolymer, a maleic-acid-N-vinyl pyrrole copolymer, Synthetic polymers (it indicates to JP,61-32787,A, 61-237680, 61-277483, etc.), such as a styrene maleic anhydride copolymer and polyethyleneimine, etc. can be mentioned. They are polyvinyl pyrrolidones, polyvinyl alcohol, and polyalkylene oxide preferably among these polymers.

[0069] As the above-mentioned polyvinyl alcohol, polymerization degree is desirable especially desirable and the range of 200–4000 is 1000–3000.

[0070] The compound shown by the above-mentioned polyalkylene oxide, for example, polyethylene oxide and polyethylene glycols, polypropylene glycols, or the following general formula (P) is mentioned.

[0071] General formula (P)

$R_3O-(A_4-O)_j$  — among  $4-(A_5-O)_j5-(A_6-O)_j6-R_4$  type, although  $A_4$ ,  $A_5$ , and  $A_6$  express the straight chain which is not permuted [ a permutation and ] or the alkylene group of branching, respectively, they do not become the same [ all ] even if  $R_3$  and  $R_4$  are the same respectively — you may differ — a hydrogen atom — the alkyl group which is not permuted [ a permutation and ], an aryl group, an acyl group, etc. are expressed, respectively.

[0072] As each substituent, a hydroxy group, a carboxy group, a sulfonyl group, an alkoxy group, a carbamoyl group, and a sulfamoyl group are mentioned. Preferably,  $R_3$  and  $R_4$  are hydrogen atoms, and  $A_4$ ,  $A_5$ , and  $A_6$  are non-permuted things, respectively. Moreover, as most desirable thing,  $A_4$ ,  $A_5$ , and  $A_6$  are  $-CH_2CH_2-$  or  $-CH(CH_3)-CH_2-$ .

[0073]  $j_4$ ,  $j_5$ , and  $j_6$  express the integer of 0, or 1–500, respectively. However, it is  $j_4+j_5+j_6 \geq 5$ .

[0074] As a thing desirable at polyalkylene oxide, it is polyethylene oxide, it is the polyethylene glycol (PEG may be called) which has average molecular weight in the range of 10,000–500,000

desirable especially preferably, and average molecular weight is the thing of the range of 50,000–300,000.

[0075] The average molecular weight of the above-mentioned polyalkylene oxide is the molecular weight computed with the hydroxyl value.

[0076] In this invention, it is desirable to apply a cross linking agent in the range which does not influence this invention as an object which constructs a bridge in a water-soluble polymer. As a concrete example of a cross linking agent, the aldehyde system compound like formaldehyde and glutaraldehyde, Diacetyl, the ketone compound like a KURORU 2,4-pentanedione, a screw (2-chloro ethylurea), 2-hydroxy – Triazine system compounds, such as 4 and 6-dichloro-1,3,5-triazine, The compound which has a reactant halogen like a U.S. Pat. No. 3,288,775 number publication, A divinyl sulfone, a carbamoyl pyridinium system compound given in JP,8-50342,A, A compound with the reactant olefin like a U.S. Pat. No. 3,635,718 number publication, N-methylol compound given in a U.S. Pat. No. 2,732,316 number, and the isocyanate like a U.S. Pat. No. 3,103,437 publication A U.S. Pat. No. 3,017,280 number and the aziridine compounds like this No. 2,983,611 publication The carbodiimide system compounds like a U.S. Pat. No. 3,100,704 number publication The epoxy compound like a U.S. Pat. No. 3,091,537 number publication, and the halogen carboxyl aldehydes like mucochloric acid inorganic cross linking agents, such as organic cross linking agents, such as a dioxane derivative like dihydroxy dioxane, chromium alum, potash alum, a sulfuric-acid zirconium, and a way acid, etc. — it is — these — one sort — or two or more sorts can be combined and it can use.

[0077] As an approach of forming the acceptance layer of this invention, the coating approaches usually used, such as the size press method, the roll coater method, the blade coating-machine method, the air knife coating-machine method, the gate roll coater method, the rod bar coating-machine method, the curtain method, the slide hopper method, and the extrusion method, are used.

[0078] In the acceptance layer of this invention, various additives with still better known fixing agent of an inorganic pigment besides a binder and a hardening agent, a coloring color, a color pigment, and an ink color, ultraviolet ray absorbent, anti-oxidant, dispersant of a pigment, defoaming agent, leveling agent, antiseptics, fluorescent brightener, viscosity stabilizer, pH regulator, etc. can also be added.

[0079] It is desirable to add a surfactant in the range which does not spoil ink absorptivity in order to raise image quality in the acceptance layer of this invention. The surface active agent used may use together the thing of the class from which a type is sufficient as both an anion system a cation system the Nonion system and a betaine system, and a low-molecular thing or the thing of a macromolecule also differs. It is the surfactant of a fluorine system preferably in these.

[0080] The above-mentioned fluorochemical surfactant For example, a U.S. Pat. No. 2,559,751 number, Said 2,567,011 numbers, said 2,732,398 numbers, said 2,764,602 numbers, Said 2,806,866 numbers, said 2,809,998 numbers, said 2,915,376 numbers, Said 2,915,528 numbers, said 2,918,501 numbers, said 2,934,450 numbers, Said 2,937,098 numbers, said 2,957,031 numbers, said 3,472,894 numbers, Said 3,555,089 numbers, British JP,1,143,927,B, said 1,130,822 numbers, JP,45-37304,B, JP,47-9613,A, 49-134614, 50-117705, 50-117727, 50-121243, 52-41182, 51-12392, British American Institute of Chemists magazine (J. Chem.Soc.) 1950 2789 pages, These the 1957 2574 pages and, 2640 pages, American-institute-of-chemists magazine (J. Amer.Chem.Soc.) 79-volume 2549 pages (1957), It is compoundable by the approach indicated by 12 oil chemistry (J. Japan Oil ChemistsSoc.) 653 pages, organic chemistry meeting magazine (J. Org.Chem.) 30-volume 3524 pages (1965), etc.

[0081] It is a trade name. a certain kind among these fluorochemical surfactants of thing — Dainippon Ink & Chemicals, Inc. to megger fuck (Megafac) F — Minnesota mining — and — MANIFAKUCHUA ring company company to Fluorad (Fluorad) FC — by the trade name MONFU from an imperial chemical industry company — a roll (Monflor) — by the trade name from I eye E. I. du Pont de Nemours NEMERASU— and — company company — Zonyls (Zonyls) — a trade name — it is — moreover, FARUPEBERUKE Hoechst A.G. to RIKOBETTO (Licowet) VPF — it is marketed by the trade name, respectively.

[0082] As an amount of coating of the acceptance layer of this invention, 5 – 100 g/m<sup>2</sup> is

desirable, and is 10 – 50 g/m<sup>2</sup> more preferably. Moreover, the range of being 10–100 micrometers as thickness of an acceptance layer is 40–70 micrometers desirable especially preferably.

[0083] All over an ink absorbing layer, an organic mat agent can be used in order to raise conveyance nature.

[0084] A mat agent may be set to a photograph technical field, is known, and can be defined as being the discontinuous particle of the organic material which can be distributed in a hydrophilic organic colloid binder.

[0085] As an example of an organic mat agent, they are starch, cellulose ester (for example, cellulose acetate propionate etc.), cellulose ether, synthetic resin (for example, ethyl cellulose etc.), etc. as the example of synthetic resin — water — insoluble or a poorly soluble composition polymer — it is — for example, alkyl (meta) acrylate — Alkoxy alkyl (meta) acrylate, glycidyl (meta) acrylate, Acrylamide, vinyl ester (for example, vinyl acetate), acrylonitrile, (Meta) Independent or combination, such as an olefin, styrene (for example, ethylene etc.), and a benzoguanamine formaldehyde condensate, Or the polymer which uses combination of these, an acrylic acid, a methacrylic acid, alpha, beta-partial saturation dicarboxylic acid, hydroxyalkyl (meta) acrylate, sulfoalkyl (meta) acrylate, a styrene sulfonic acid, etc. as a monomer component can be used.

[0086] In addition, an epoxy resin, nylon, a polycarbonate, phenol resin, a polyvinyl carbazole, a polyvinylidene chloride, etc. can be used.

[0087] 3–20 micrometers has [ these mat agent ] the viewpoint of conveyance nature to a desirable weighted mean particle size, and, as for the AUW in an acceptance layer (it is attached and is also called an amount), it is desirable that it is 10 – 100 mg/m<sup>2</sup>, and it is desirable to eliminate beforehand a particle 3 micrometers [ or less ] and a particle 20 micrometers or more by the classification from the point of coating liquid ammonia quality. Moreover, these mat agent can also be used together.

[0088] The record form for ink jet printers concerning this invention means not only paper but all the so-called ink jet record material, record material puts the thing which carried out coating on the base material or which was made to contain, and things, such as a front face of the shape of a sheet and not only tabular but a can, etc. can be especially used without a limit as a base material. Moreover, also with a transparent base material, also with an opaque base material, it can respond in activity eye and can use.

[0089] As a transparent base material, each well-known thing can use it conventionally, for example, there are a film thru/or a sheet, or glass plates, such as polyester resin, cellulose acetate resin, acrylic resin, polycarbonate resin, polyvinyl chloride resin, polyimide resin, cellophane, and celluloid, etc. The viewpoint of the rigidity of a base material and transparency to polyester resin, especially a polyethylene terephthalate film are desirable in these.

[0090] As an opaque base material, these complex, such as films, such as coated paper, such as non-coated paper, such as paper of fine quality, a report grade paper, super can lender processing paper, a \*\*\*\* stencil, and tracing paper, art paper, coat paper, a light weight coat paper, fine coated paper, and a cast-coated paper, a plastic film, an opaque film containing a pigment, and a foaming film, resin coat paper, an impregnated paper, a nonwoven fabric, cloth, a metal film, and a metal plate, can be used.

[0091] In these, the resin coat paper from a viewpoint of glossiness and smooth nature and various films are desirable, and the film of a polyester system is more desirable in polyolefin resin coat paper and various films in resin coat paper from a feeling of a feel, and a high-class feeling.

[0092] Although the paper which especially a limit does not have the stencil which constitutes the resin coat paper used preferably, and is generally used can be used, a smooth stencil which is used for the base material for photographs more preferably is desirable. as the pulp which constitutes a stencil — natural pulp, playback pulp, a synthetic pulp, etc. — one sort — or two or more sorts are mixed and it is used. Additives, such as the sizing compound generally used of paper making, a paper reinforcing agent, a loading material, an antistatic agent, a fluorescent brightener, and a color, are blended with this stencil.

[0093] Furthermore, a surface sizing compound, a surface paper durability agent, the fluorescent brightener, the antistatic agent, the color, the anchoring agent, etc. may be applied to the front face.



[0094] Moreover, although there is especially no limit about the thickness of a stencil, the good thing of the surface smooth nature which impressed paper under paper milling or in the calender after paper milling, and compressed the pressure is desirable.

[0095] As resin of resin coat paper, the resin hardened with polyolefin resin or an electron ray can be used. As polyolefin resin, it is the copolymers which consist or more of two of olefins, such as a homopolymer of olefins, such as low density polyethylene, high density polyethylene, polypropylene, polybutene, and the poly pentene, or ethylene propylene rubber, and such mixture, and the thing of various kinds of consistencies and various kinds of melt viscosity characteristics (melt index) can be used for independent or them, mixing.

[0096] In the resin of resin coat paper, moreover, white pigments, such as titanium oxide, a zinc oxide, talc, and a calcium carbonate, Fatty-acid amides, such as octadecanamide and an arachidic acid amide, zinc stearate, Fatty-acid metal salts, such as calcium stearate, aluminum stearate, and magnesium stearate, Antioxidants, such as IRUGA NOx 1010 and IRUGA NOx 1076, Blue pigments and colors, such as cobalt blue, ultramarine blue, sicilian blue, and a copper phthalocyanine blue, It is desirable to add combining suitably various kinds of additives, such as a pigment of Magentas, such as cobalt violet, fast violet, and manganese purple, a color, a fluorescent brightener, and an ultraviolet ray absorbent.

[0097] The base material used by this invention is JIS. Since the thing of continuation conveyance nature of 1 – 15 g-cm improves to the environmental variation of temperature and humidity, the Taber stiffness by P-8125 is used especially preferably.

[0098] The ink jet record approach of this invention is the recording device outputted using different ink beyond \*\*5 sort. recording on the record material of this invention, and \*\* — to at least one sort of criteria colors with the recording device recorded in two or more sorts of different ink Recording on the record material of this invention or the \*\* aforementioned criteria color is characterized by what is recorded with the recording device recorded in two or more sorts of ink in which the absorbances of the ink of this criteria color differ substantially.

[0099] The ink jet record approach that the ink jet record approach used for this invention records water on the record sheet for ink jets of this invention in the ink contained 40% of the weight or more is used preferably, and the following coloring agent, a solvent object, and the ink jet record liquid that consists of other additives are used for this ink. As a coloring agent, water soluble dye, such as direct dye, acid dye, basic dye, reactive dye, or a food dye, is mentioned.

[0100] As a solvent of the ink used for the acceptance layer of this invention Water and water-soluble, various organic solvents, for example, methyl alcohol, ethyl alcohol, Propyl alcohol, isopropyl alcohol, butyl alcohol, Alkyl alcohols of the carbon numbers 1-4 of sec-butyl alcohol, tert-butyl alcohol, isobutyl alcohol, etc.; Dimethylformamide, Amides, such as dimethylacetamide; Ketones, such as an acetone and diacetone alcohol, or a ketone-alcohol; tetrahydrofuran, Ether, such as dioxane; Polyalkylene glycols; ethylene glycol, such as a polyethylene glycol and a polypropylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, 1, 2, 6-hexane triol, thiodiglycol, hexylene glycol, alkylene groups, such as a diethylene glycol, — 2-6 alkylene glycol; — a glycerol — Ethylene glycol methyl ether, the diethylene-glycol methyl (or ethyl) ether, Pyrrolidones, such as pyrrolidinone, such as low-grade alkyl ether of polyhydric alcohol, such as triethylene glycol and the monomethyl ether, and 2H-pyrrolidinone, a 1-methyl-2-pyrrolidone, and 2-pyrrolidone, are mentioned. Also in the water-soluble organic solvent of these many, the low-grade alkyl ether of polyhydric alcohol, such as polyhydric alcohol, such as a diethylene glycol, the triethylene glycol monomethyl ether, and the triethylene glycol monoethyl ether, and pyrrolidones are desirable.

[0101] Although it is desirable to use the mixed solvent of water and said organic solvent from a viewpoint of clogging prevention of an ink head nozzle as for the solvent of ink, at this time, the content to the ink of water is 40 % of the weight or more, and is 50 – 90 % of the weight preferably.

[0102] As an additive to other ink, a pH regulator, a sequestering agent, an antifungal agent, a viscosity controlling agent, a surface tension regulator, a wetting agent, a surfactant, a rust-proofer, etc. are mentioned, for example.

[0103] Moreover, in this invention, if it records with the recording device which used shade ink, the effectiveness of this invention will show up notably. For example, although the conventional color

recording device has the approach in use of using one kind each of ink to four criteria colors, Y, M, C, and K, when two or more sorts of ink is used about a certain criteria color, it can improve the formation of many gradation, and the feeling of a rough deposit of the low concentration section. especially a certain criteria color (for example, Y, M, C, K) is using the ink (shade ink) in which two or more kinds of absorbances' differ, the low concentration section reduces a feeling of a rough deposit mainly using light-colored (an absorbance — low) ink, and the high concentration section mainly uses the ink of a dark color (an absorbance — high), and a configuration out of which sufficient maximum concentration comes is known. Light color ink and dark color ink may be using the same color, and even if it is using a different color, the combination of the color from which plurality differs is also available. as the recording device which is using shade ink about such a criteria color — PM-700 — C (Seiko Epson), Picty300 (NEC), and Photo It is marketed by the trade name of Smart (Hewlett Packard), and it is the description to output in a total of six sorts of ink of the ink of light-colored M and light-colored C other than Y, M, C, and K. Moreover, BJC-700J (canon company make) are mentioned as an example of the recording device of the same method.

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[Translation done.]

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2. \*\*\*\* shows the word which can not be translated.

3. In the drawings, any words are not translated.

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**EXAMPLE**

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[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to these.

[0105] The base material which carried out 20 g/m<sup>2</sup> coating of the resin constituent which becomes the front face of the base material of <production of base material> basis weight 60 g/m<sup>2</sup> from the low-density-polyethylene 70 section and the high-density-polyethylene 20 section, and carried out 20g/[m ] 2 coating of the resin constituent which becomes a rear face from the low-density-polyethylene 50 section was produced.

[0106] The 4 opening flask which is 300ml of composition of colloidal silica by which <composition (1) of non-subtlety particle (polymer joint inorganic particle) which organic cationic polymer combined> surface treatment was carried out was equipped with the agitator, and 100g (the content of a silica is 20%) was supplied for colloidal silica (the trade name Snow tex OUP, the Nissan chemistry company make). 3-methacryloxy propyl trimethoxysilane was dropped at this, stirring 1.0g and 10g of distilled water. It was made to react at a room temperature furthermore for 30 minutes, and the target colloidal silica by which surface treatment was carried out was obtained as a distributed object.

[0107] (2) The 4 opening flask of 2l. of composition of an intermediate-product particle was equipped with an agitator, a thermometer, gas installation tubing, and a capacitor, 200g and a surfactant (trade name TORAKKUSU H-45) were thrown in for distilled water, and 7.7g and a potassium hydroxide were thrown in for 0.78g. Nitrogen gas was stirred for 30 minutes at the room temperature with the sink, and was deaerated. 12.1g and a divinylbenzene were supplied for styrene, 12.9g was supplied for 0.8g and dimethylamino methyl styrene to this, and 13.7g of dispersion liquid of the colloidal silica which carried out surface treatment by the above (1) further was added. It heated until inside \*\* became 70 degrees C, stirring by per minute 300 revolution, and 0.84g (iso cyano valeric acid) of 2 and 2'-azobis was added after that. The polymerization of the heating stirring was then performed and carried out under the nitrogen air current for 5 hours.

[0108] After reaction termination, after removing unnecessary solid content using a glass filter, the intermediate-field particle made into the object was obtained as an opaque white chromatism object.

[0109] (3) The 4 opening flask of 300ml of composition of a polymer joint inorganic particle (1) was equipped with the agitator, and 100g of intermediate-field particles compounded above (2) was supplied. It was dropped stirring to this having acetonitrile 30 bet it for 30 minutes. Furthermore 3.1g of benzyl chlorides was dropped, and heating stirring was carried out in the 60-degree C oil bath for 6 hours. After reaction termination, after cooling radiationally to a room temperature, about 40ml of bottom solvents of reduced pressure was distilled out. Distilled water was added to the remaining liquid and the polymer joint inorganic particle (1) which adjusts the whole to 100g and is made into the object was obtained as an opaque white chromatism object.

[0110] (4) While using as the compound of table 1 publication the non-subtlety particle by which surface treatment is carried out, the ratio of each monomer was made into the value of a publication among an instantiation compound, and also it is an instantiation compound (2) by the same actuation, The polymer joint inorganic particle (1) which has (3), (4), (7), (8), and (10) in a mother nucleus, (2), (3), (4), (7), (8), and (10) were compounded.

[0111] The polymer joint inorganic particle created by the example 1 – the 13 above-mentioned approach (1), The coating liquid which carried out 12 weight sections addition of the polyvinyl alcohol polymerization degree 2500 (PVA may only be called below) for (2), (3), (4), (7), (8), and (10) 98% whenever [ 88 weight sections and saponification ] was created, coating was carried out so that desiccation solid content might be set to 20g/m<sup>2</sup> with a wire bar, and the sample was created.

[0112] The coating liquid which carried out 12 weight sections addition of the polyvinyl alcohol degree of polymerization 2500 for one to example of comparison 3 colloidal silica, alumina sol, and a zinc oxide 98% whenever [ 88 weight sections and saponification ], respectively was created, coating was carried out so that desiccation solid content might be set to 20g/m<sup>2</sup> with a wire bar, and the sample was created.

[0113] Example of comparison 4 polymerjournal, vol.21, No.6, p475 (1989), and Journal of The non-subtlety particle which graft-ized acrylate by using a silica as a nucleus polymerscience, A, vol.29, p697 (1992), a front face, vol.30, No.1, p74 (1992), etc. according to the approach of a publication was created. Then, the coating liquid which carried out 12 weight sections addition of the polyvinyl alcohol degree of polymerization 2500 for the created non-subtlety particle 98% whenever [ 88 weight sections and saponification ] was created, coating was carried out so that desiccation solid content might be set to 20g/m<sup>2</sup> with a wire bar, and the sample was created.

[0114] Next, the following approaches estimated the sample created in the above-mentioned examples 1–13 and the examples 1–4 of a comparison. At this time, all assessment was outputted using Seiko Epson ink jet printer PM700C. Moreover, as an output environment at this time, it carried out in 25 degrees C and the environment of 70%RH except for generating of a crack supposing the rainy season term.

[0115] The sample <generating of a crack> Obtained was judged to 210mmx297mm(A4), ten samples with a bore of 30mm stopped on the tape were produced [ it rounded off to the longitudinal direction so that it might become cylindrical, and ], and it was left for one week by 15 degrees C and 20% environment. then, 5 or 6 random per sheet — the 10mmx10mm range — determining — the number of a crack — an optical microscope — measuring — A4 — the number of average cracks was made into the number of cracks per sheet.

[0116] <Bleeding> SCID N3 image was printed and the lap of the dot of cyanogen-Magenta and Magenta-yellow and yellow-cyanogen was observed with the optical microscope.

O; most color muddiness was not observed but the image also with high sharp nature was obtained.

O; an image is satisfactory level although color muddiness of some arises only into a cyanogen-Magenta part.

\*\*; color muddiness is in a cyanogen-Magenta and Magenta-yellow part, and the red part of an image can be seen in the shape of nonuniformity.

x; color muddiness has arisen in the total color and it became the image which faded on the whole.

[0117] <Beading> yellow, a Magenta, cyanogen, black, Green, blue, and the maximum-density section of red were outputted, and viewing estimated the rough deposit degree.

O; there is no rough deposit in each color, and excel in it.

O; although few rough deposits are checked by the Green section, it is not actual harm level.

\*\*; a rough deposit is checked by the Green section and the blue section.

x; on the whole, a rough deposit is severe and is not set to goods level.

[0118] After having outputted the natural image of <drying> A4 size, having rounded off so that it might become the bore of 4cm about a form after 10 minutes, and stopping on a tape, the sample was observed one day after and viewing estimated the imprint degree on the back.

[0119] O; completely with no imprint.

O; with [ although there is an imprint slightly ] no practical skill top problem.

\*\*; an imprint occurs in the high concentration section.

x; an imprint occurs and the film peels from an imprint side.

[0120]

[A table 1]

	有機がわ性シリカ 無機微粒子	有機がわ性シリカに結合した無機微粒子 有機がわ性シリカ	有機がわ性シリカ 無機微粒子比	受容層中の 含有率(重量%)	アクリル酸 ビニール	乾燥性	クラックの発生 (個/A4サイズ)
実施例 1	コロイダルシリカ *1	例示化合物(1)	0.5/99.5	88	◎~○	◎	2
実施例 2	コロイダルシリカ *1	例示化合物(2)	0.5/99.5	88	◎~○	◎	1
実施例 3	コロイダルシリカ *1	例示化合物(3)	0.5/99.5	88	◎~○	◎	2
実施例 4	コロイダルシリカ *1	例示化合物(4)	0.5/99.5	88	◎~○	◎	1
実施例 5	コロイダルシリカ *1	例示化合物(7)	0.5/99.5	88	◎~○	◎	1
実施例 6	コロイダルシリカ *1	例示化合物(8)	0.5/99.5	88	◎~○	◎	1
実施例 7	コロイダルシリカ *1	例示化合物(10)	0.5/99.5	88	◎~○	◎	2
実施例 8	酸化シリカ	例示化合物(3)	0.5/99.5	88	◎	◎~○	5
実施例 9	アクリル	例示化合物(3)	0.5/99.5	88	◎	◎	4
実施例 10	酸化亜鉛	例示化合物(3)	0.5/99.5	88	◎	◎	7
実施例 11	酸化シリカ	例示化合物(3)	0.5/99.5	88	◎	◎	7
実施例 12	非晶質シリカ *3	例示化合物(3)	0.5/99.5	88	◎~○	◎	1
実施例 13	酸化シリカ *2	例示化合物(3)	0.5/99.5	88	◎	◎	8
比較例 1	コロイダルシリカ *2	未結合	0.5/99.5	88	△~×	△	21
比較例 2	酸化亜鉛	未結合	0.5/99.5	88	△~×	△	33
比較例 3	アクリル	未結合	0.5/99.5	88	△	△	20
比較例 4	コロイダルシリカ	アクリルシリカ	0.5/99.5	88	◎	△	35

コロイダルシリカ \*1 日産化学社製スノーテックス OUP

コロイダルシリカ \*2 日産化学社製スノーテックス O

非晶質シリカ \*3 日本 AEROSIL 社製 AEROSIL 200

As shown also in a table 1, the record form for ink jet printers of this invention prevents generating of a crack, and under a high-humidity condition, drying can be raised, and a high definition image can be obtained by high concentration, and it also turns out that a good result is shown.

[0121] Using the colloidal silica (the Nissan chemistry company make; Snow tex OUP) and the instantiation compound 3 which were used in the 14 to example 29 example 3, adjust an organic cationic polymer / non-subtlety particle ratio so that it may become the value of table 2 publication, and adjust the amount of the polymer joint inorganic particle in coating liquid, and the content in an acceptance layer was made to become the value of table 2 publication, and also it is the same actuation. It evaluated by creating a sample. The following assessment was added at this

time.

[0122] After performing the same assessment as generating of a <mustache-like myogenesis> crack, the alphabet (26 characters) surplus was printed all over the sample, and the muscle of the shape of a mustache generated on a character boundary line was observed visually.

O; generating of a mustache-like muscle was not seen at all.

O; less than five generating is level which is satisfactory at all on practical skill, although it saw.

Level which generating of \*\*;5-30 place is checked and is a little conspicuous.

Generating beyond x;30 place is checked and it is problematic level on practical skill.

[0123] <Glossiness after printing> yellow, a Magenta, cyanogen, black, Green, blue, and the maximum-density section of red were outputted, and after getting dry enough, glossiness was checked visually.

O; each color is maintaining glossiness.

O; the other colors of a falling [ the glossiness of the black section ]-a little thing are maintaining glossiness, and are level which is satisfactory at all on practical skill.

\*\*; although it is the level in which glossiness is inferior a little on the whole, and concentration is also a little inferior, actual harm nature has no problem.

x; there is no glossiness in each color and it is problem level.

[0124]

[A table 2]

	有機がわ <sup>ポ</sup> リス ／無機微粒子比	受容層中の 含有率(重量%)	ポリデインク <sup>+</sup>	ビデインク <sup>+</sup>	乾燥性	膜上のスジ <sup>+</sup>	印字部の 光沢性
実施例 14	0.5/99.5	88	◎〜○	○	◎	○	○
実施例 15	10/90	88	◎	◎〜○	◎	◎〜○	◎
実施例 16	20/80	88	◎	◎	◎	◎	◎
実施例 17	50/50	88	◎	◎	◎	◎	◎
実施例 18	80/20	88	◎	◎	◎	◎	◎
実施例 19	90/10	88	◎	◎	◎	◎	◎
実施例 20	99.5/0.5	88	○	○	○	◎〜○	○
実施例 21	20/80	5	○	○	○	○	○
実施例 22	20/80	10	◎〜○	◎〜○	◎〜○	◎〜○	◎〜○
実施例 23	20/80	30	◎〜○	◎〜○	◎〜○	◎〜○	◎〜○
実施例 24	20/80	50	◎	◎	◎	◎	◎
実施例 25	20/80	70	◎	◎	◎	◎	◎
実施例 26	20/80	99	◎	◎	◎	◎	◎
実施例 27	20/80	100	◎〜○	◎〜○	◎〜○	○	◎
実施例 28	1/99	88	◎	◎〜○	◎	◎〜○	○
実施例 29	99/1	88	◎〜○	◎〜○	◎〜○	◎〜○	○

[0125] It turns out that the result with the good time of an organic cationic polymer / non-subtlety particle ratio being 99/1 or less [ 1/99 or more ] is shown as shown in a table 2, and a still better result is shown when the content in an acceptance layer is 10 - 99 % of the weight.

[0126] Although the sample created in the example 30 examples 1-29 was replaced with Seiko Epson ink jet printer PM700C and performed in Deskjet 2000C made from Hewlett Packard, the almost same result was obtained and it was checked that the effectiveness of this invention is demonstrated enough.

[0127]

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(54) 【発明の名称】 インクジェットプリンター用記録用紙及び記録方法

(57) 【要約】

【課題】 高速、多吐出量プリンターやロールプリンターで生じている画質の劣化（ビーディング、ブリーディングなど）や乾燥性の劣化、クラックの発生や印字部と未印字部の境界に生じる髭状の筋の発生を解決する。

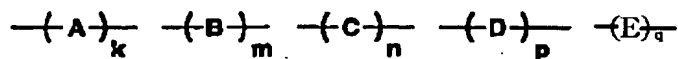
【解決手段】 受容層中に有機カチオン性ポリマーが結合した無機微粒子を含有することを特徴とするインクジェットプリンター用記録用紙である。



## 【特許請求の範囲】

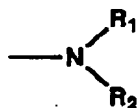
【請求項 1】受容層中に有機カチオン性ポリマーが結合した無機微粒子を含有することを特徴とするインクジェットプリンター用記録用紙。

【請求項 2】前記有機カチオン性ポリマーが下記一般式一般式 (I)

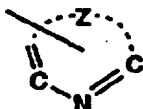


一般式 (I) において (A) は第四級アンモニウム基を有する共重合可能なモノマーを重合したモノマー単位を表し、(B) は下記一般式 (II)、(III)、(IV) 及び (V) で表される構造のうち少なくとも一つ含

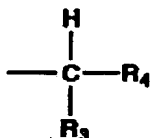
## 一般式 (II)



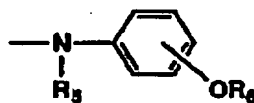
## 一般式 (III)



## 一般式 (IV)



## 一般式 (V)



一般式 (II) において R<sub>1</sub> 及び R<sub>2</sub> は脂肪族基を表し、一般式 (III) においては Z は  $\text{---C---N=C---}$  と共同して五員又は六員環を形成するのに必要な非金属原子群を表す。一般式 (IV) において R<sub>3</sub> 及び R<sub>4</sub> は芳香族基、ハロゲン原子、シアノ基及びオキシカルボニル基を表す。一般式 (V) においては R<sub>5</sub> は水素原子及び脂肪族基を表し、R<sub>6</sub> は脂肪族基を表す。上記一般式

(I) において (C) は少なくとも二個のエチレン状不飽和結合基を有する共重合可能なモノマーを重合したモノマー単位を表し、(D) は (A)、(B)、及び

(I) で表される化合物から構成されることを特徴とする請求項 1 記載のインクジェットプリンター用記録用紙。

## 【化 1】

10 有する共重合可能なモノマーを重合したモノマー単位を表す。

## 【化 2】

(C) 以外の共重合可能なモノマーを重合したモノマー単位を表す。上記一般式 (I) において、(E) で表されるモノマー単位は前記無機微粒子と共有結合を形成する基を有するモノマー単位を表す。k は 10 から 95 モル%、m は 0 から 30 モル%、n は 0 から 10 モル%、p は 0 から 80 モル%、および q は 0.1 から 20 モル%を表す。但し、k、m、n、p、q の合計は 100 モル%である。

【請求項 3】前記無機微粒子に対する有機カチオン性ポリマー重量比 (有機カチオン性ポリマー/無機微粒子)

が1/99以上99/1以下であることを特徴とする請求項1又は2記載のインクジェットプリンター用記録用紙。

【請求項4】前記有機カチオン性ポリマーが結合した無機微粒子が、受容層中に10～99重量%含有していることを特徴とする請求項1～3のいずれかに記載のインクジェットプリンター用記録用紙。

【請求項5】支持体がポリオレフィン被覆紙であることを特徴とする請求項1～4のいずれかに記載のインクジェットプリンター用記録用紙。

【請求項6】5種以上の異なるインクを使用して出力する記録装置で、請求項1～5のいずれかに記載の記録用紙に記録することを特徴とするカラーインクジェット記録方法。

【請求項7】少なくとも1種の基準色に対して、2種以上の異なるインクにより記録する記録装置で、請求項1～5のいずれかに記載の記録用紙に記録することを特徴とするカラーインクジェット記録方法。

【請求項8】前記基準色が、該基準色のインクの吸光度が実質的に異なる2種以上のインクにより記録する記録装置で記録することを特徴とする請求項7記載のカラーインクジェット記録方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、各種のインクジェットプリンター方式に適用できるインクジェットプリンター用記録用紙及び記録方法に関するものである。

【0002】

【従来の技術】インクジェット記録装置（本明細書において、インクジェットプリンターとも言う。但し、いわゆるプリンターに限定されない記録装置の全般に、本発明は適用できることは勿論である。）は、騒音が少なく、高速印字が可能であり、また、複数のインクノズルを使用することにより多色記録を行うことも容易であることから、特にコンピューター用の画像情報出力装置として近年急速に普及している。

【0003】また、フルカラー記録用に開発されたインクジェットプリンターの中には、銀塩写真方式のカラー画像に匹敵するほどの高画質な画像を出力できるものもある。また、出力する画像の内容も、文字や図形などから写真に近い画質が要求されるカラー版下やデザインイメージ等へと拡大している。

【0004】従って、その記録媒体としては、光沢性や濃度の低くなるコート紙や普通紙よりもむしろ、より写真に近い光沢性を有する不透明なフィルムや光沢のでる樹脂被覆紙を利用した光沢紙又は光沢フィルムや、或いはコート紙の表面をキャストして鏡面光沢性を持たせたキャストコート紙などが多く用いられるようになってきた。

【0005】これらに対応し、インク受容層（又はコー

ト層）としては、水性インクを膨潤又は溶解する水溶性ポリマーを用いることが提案されている。例えば、特開昭62-263084号では特定pHのゼラチン水溶液から形成された受容層が、特開平6-64306号では塗布したゼラチンを一旦ゲル状態にした後、コールドドライ法により乾燥させて得られるインクジェットプリンター用記録シートが、特開昭62-214985号では平均分子量が $5 \times 10^4$ 以上のポリエチレンオキサイドを含有する受容層がそれぞれ提案されている。

10 【0006】また一方で、無機微粒子を用いた多孔質型の受容層が提案されている。多孔質型の受容層は微粒子により微細な空隙を設け、インクを受容するもので、乾燥性は非常に優れており、色濁りも少なく、高解像度の画像が出力できるという利点を有している。

【0007】ところが近年、高速、多吐出量インクジェットプリンターの出現により、プリント速度やインク吸収容量が対応できず、ドット間で色濁り（ブリーディング）やビーディング（マダラ）が生じ、高品質な画像を得ることができなくなってきた。また、更にこれらのプリンターは濃淡インクを用いることにより多階調を実現していることから、インク量が増加し、特に高湿条件では乾燥不良なども多発し、深刻な問題となってきた。これらの問題を解決するため、吸収容量を増大させる手段として受容層の厚みを厚くする方法があるが、逆に搬送不良が生じたり、コストアップにつながり、好ましくない。更に、多孔質型受容層は無機微粒子を用いているため、受容層自体の膜強度が高く、伸延性が低いためにクラック（亀裂）が生じやすいという問題点も有していることが分かった。

30 【0008】これらの問題点はロールプリンター用として適用する場合、更に大きな問題となってくる。例えばロールプリンターを使用する分野としてポスター等を作成する出力センターがあるが、通常、文字の鮮鋭性やコントラストをよくするためにRIPと呼ばれるカラーバランス調整手段により、インク量を増大させ、使用することが一般的に用いられるため、上記のような問題はアマチュアユーザーが使用するデスクトップ型プリンターより更に発生しやすいのが現状である。製品形態としてもロール状に強く巻き付けられているのでクラックは生じやすく、その部分に印字されるとクラックに沿って髭状にインクが流れ出し、画像品質が劣化する問題が生じる。また、大抵のユーザーは印字後、丸めて長期間保管するので乾燥性が劣化すると、裏面に転写することもあり、品質を損なう恐れがある。ロールプリンターを使用するユーザーはプロユーザーがほとんどであり、これらの問題を解決しなければ使用できないのが現状である。

【0009】

【発明が解決しようとする課題】本発明の目的は、上述した近年急速に増加している高速、多吐出量プリンターやロールプリンターで生じている画質の劣化（ビーディ

ング、ブリーディングなど)や乾燥性の劣化、クラックの発生や印字部と未印字部の境界に生じる髭状の筋の発生を解決するインクジェットプリンター用記録用紙及び記録方法を提供することにある。

# 【0010】

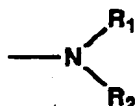
【課題を解決するための手段】本発明の上記課題は、

1. 受容層中に有機カチオン性ポリマーが結合した無機微粒子を含有することを特徴とするインクジェットプリンター用記録用紙、

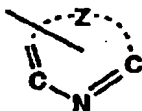
2. 前記有機カチオン性ポリマーが下記一般式 (I) で表される化合物から構成されることを特徴とする前記 1 記載のインクジェットプリンター用記録用紙、

# 【0011】

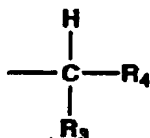
## 一般式 (II)



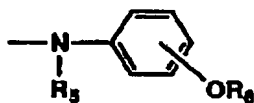
## 一般式 (III)



## 一般式 (IV)



## 一般式 (V)

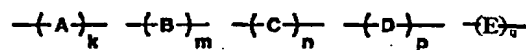


【0014】一般式 (II) において  $\text{R}_1$  及び  $\text{R}_2$  は脂肪族基を表し、一般式 (III) においては  $\text{Z}$  は  $\text{---C---N=C---}$  と共同して五員又は六員環を形成するのに必要な非金属原子群を表す。一般式 (IV) において  $\text{R}_3$  及び  $\text{R}_4$  は芳香族基、ハロゲン原子、シアノ基及びオキシカルボニル基を表す。一般式 (V) においては  $\text{R}_5$  は水素原子及び脂肪族基を表し、 $\text{R}_6$  は脂肪族基を表す。

【0015】上記一般式 (I) において (C) は少なくとも二個のエチレン状不飽和結合基を有する共重合可能なモノマーを重合したモノマー単位を表し、(D) は

# 【化3】

## 一般式 (I)



【0012】一般式 (I) において (A) は第四級アンモニウム基を有する共重合可能なモノマーを重合したモノマー単位を表し、(B) は下記一般式 (II)、(III)、(IV) 及び (V) で表される構造のうち少なくとも一つ含有する共重合可能なモノマーを重合したモノマー単位を表す。

# 【0013】

## 【化4】

(A)、(B)、及び (C) 以外の共重合可能なモノマーを重合したモノマー単位を表す。

【0016】上記一般式 (I) において、(E) で表されるモノマー単位は前記無機微粒子と共有結合を形成しうる基を有するモノマー単位を表す。

【0017】 $k$  は 10 から 95 モル%、 $m$  は 0 から 30 モル%、 $n$  は 0 から 10 モル%、 $p$  は 0 から 80 モル%、および  $q$  は 0.1 から 20 モル%を表す。但し、 $k$ 、 $m$ 、 $n$ 、 $p$ 、 $q$  の合計は 100 モル%である。

【0018】3. 前記無機微粒子に対する有機カチオン

性ポリマー重量比（有機カチオン性ポリマー／無機微粒子）が 1/99 以上 99/1 以下であることを特徴とする前記 1 又は 2 記載のインクジェットプリンター用記録用紙、

4. 前記有機カチオン性ポリマーが結合した無機微粒子が、受容層中に 10～99 重量%含有していることを特徴とする前記 1～3 のいずれかに記載のインクジェットプリンター用記録用紙、

5. 支持体がポリオレフィン被覆紙であることを特徴とする前記 1～4 のいずれに記載のインクジェットプリンター用記録用紙、

6. 5 種以上の異なるインクを使用して出力する記録装置で、前記 1～5 のいずれかに記載の記録用紙に記録することを特徴とするカラーインクジェット記録方法、

7. 少なくとも 1 種の基準色に対して、2 種以上の異なるインクにより記録する記録装置で、前記 1～5 のいずれかに記載の記録用紙に記録することを特徴とするカラーインクジェット記録方法、

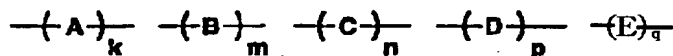
8. 前記基準色が、該基準色のインクの吸光度が実質的に異なる 2 種以上のインクにより記録する記録装置で記録することを特徴とする前記 7 記載のカラーインクジェット記録方法、の各々により達成される。

【0019】

【発明の実施の形態】本発明について更に詳細に説明する。先ず本発明に用いられる有機カチオン性ポリマーが結合した無機微粒子について説明する。

【0020】本発明に用いられる無機微粒子は微細な粒径を有する粒子であり、例えばカオリン（白土）、タルク、酸化チタン、酸化亜鉛、酸化ジルコニウム、酸化セリウム、酸化イットリウム、酸化スズ、酸化アンチモン

#### 一般式 (I)



【0027】一般式 (I) において (A) は第四級アンモニウム基を有する共重合可能なモノマーを重合したモノマー単位を表し、(B) は一般式 (II)、(III)、(IV)、及び (V) で表される構造のうち少な

ゾル、酸化ニオブゾル、ケイ酸アルミニウム、水酸化アルミニウム、酸化アルミニウム、ケイ酸カルシウム、ケイ酸マグネシウム、コロイダルシリカ、あるいは非晶質シリカ等が挙げられる。

【0021】これらの中で特に好ましくは酸化アルミニウム、コロイダルシリカ、非晶質シリカ、酸化亜鉛、酸化チタンが挙げられる。これら無機微粒子の形状には特に制限はないが、好ましくは球形、立方形、棒状、針状、鎖状、環状、平板状等が挙げられる。平均粒径としては 1～500 nm の範囲が好ましい。

【0022】これらの無機微粒子は以下に述べる有機カチオン性ポリマーにより結合されており、無機微粒子に対する有機カチオン性ポリマーの重量比（有機カチオン性ポリマー／無機微粒子）は 1/99 以上 99/1 以下の範囲であることが好ましく、さらに好ましくは 10/90 以上 90/10 以下範囲であり、特に好ましくは 20/80 以上 80/20 以下の範囲である。

【0023】本発明において有機カチオン性ポリマーが結合した無機微粒子とは有機カチオン性ポリマー内に無機微粒子と連結できる反応基が無機微粒子に選択的に結合されている状態のことを意味し、好ましくは被覆されている状態のことである（以下これらの微粒子のことをポリマー結合無機微粒子と称することもある）。

【0024】次に本発明において用いられる有機カチオン性ポリマーについて説明する。

【0025】本発明において用いられる有機カチオン性ポリマーは、好ましくは以下の一般式 (I) で表される単位を有するものである。

【0026】

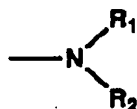
【化 5】

くとも一つ含有する共重合可能なモノマーを重合したモノマー単位を表す。

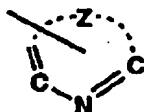
【0028】

【化 6】

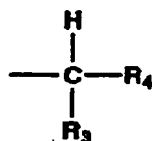
## 一般式 (II)



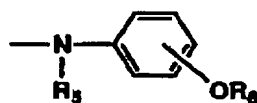
## 一般式 (III)



## 一般式 (IV)



## 一般式 (V)



【0029】一般式 (II) において  $\text{R}_1$  及び  $\text{R}_2$  は脂肪族基を表し、一般式 (III) においては  $\text{Z}$  は  $\text{---C---N=C---}$  と共同して五員又は六員環を形成するのに必要な非金属原子群を表す。一般式 (IV) において  $\text{R}_3$  及び  $\text{R}_4$  は芳香族基、ハロゲン原子、シアノ基、及びオキシカルボニル基を表す。一般式 (V) においては  $\text{R}_5$  は水素原子及び脂肪族基を表し、 $\text{R}_6$  は脂肪族基を表す。

【0030】上記一般式 (I) において (C) は少なくとも二個のエチレン状不飽和結合基を有する共重合可能なモノマーを重合したモノマー単位を表し、(D) は (A)、(B)、及び (C) 以外の共重合可能なモノマーを重合したモノマー単位を表す。

【0031】上記一般式 (I) において、(E) で表されるモノマー単位は本発明に用いられる無機微粒子と共有結合を形成しうる基を有するモノマー単位を表す。

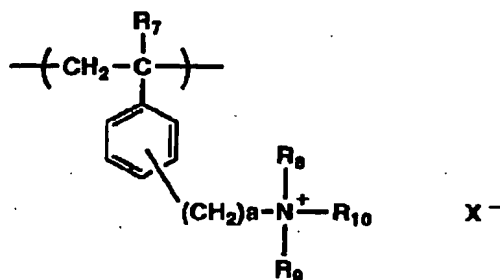
【0032】 $k$  は 10 から 95 モル%、 $m$  は 0 から 30 モル%、 $n$  は 0 から 10 モル%、 $p$  は 0 から 80 モル%、および  $q$  は 0.1 から 20 モル%を表す。

【0033】上記一般式 (I) において、(A) は以下の一般式 (VI)、(VII)、(VIII) 及び (IX) で表されるモノマー単位が好ましい。

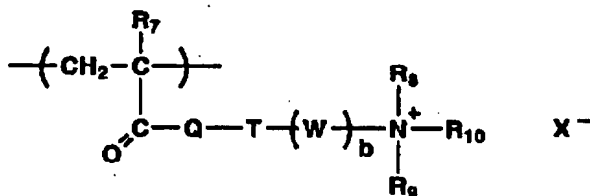
【0034】

【化7】

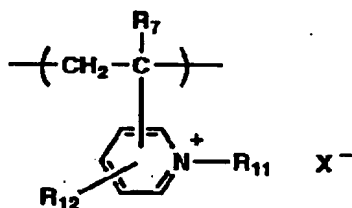
一般式 (VI)



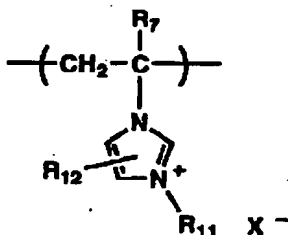
一般式 (VII)



一般式 (VIII)



一般式 (IX)



30

【0035】上記一般式 (VI)、(VII)、(VIII) 及び (IX) において R<sub>7</sub> は水素原子又は炭素原子数 1 から 4 の脂肪族基 (例えばメチル基、エチル基、n-ブチル基等) を表す。R<sub>7</sub> としては水素原子又はメチル基が好ましい。

【0036】上記一般式 (VI)、(VII)、(VIII) 及び (IX) において R<sub>8</sub>、R<sub>9</sub>、R<sub>10</sub> 及び R<sub>11</sub> は炭素原子数 1 から 10 の脂肪族基 (例えばメチル基、エチル基、シクロヘキシル基、ベンジル基等) を表す。これら R<sub>8</sub>、R<sub>9</sub>、及び R<sub>10</sub> で表される置換基は互いに同一であっても異なってもよく、また互いに結合して環状構造を形成しても良い。R<sub>8</sub>、R<sub>9</sub>、及び R<sub>10</sub> として好ましくはメチル基、エチル基、及びベンジル基であり、メチル基及びベンジル基が特に好ましい。

【0037】上記一般式 (VI)、(VII)、(VIII) 及び (IX) において X は陰イオンを表し、例えばハロゲンイオン (例えば塩素イオン、臭素イオン、ヨウ素イオン等)、アルキル硫酸イオン (例えばメチル硫酸イオン等)、アルキルあるいはアリールスルホン酸イ

オン (例えばメタンスルホン酸イオン、p-トルエンスルホン酸イオン等)、及び酢酸イオン等が挙げられる。このうちハロゲンイオン及びアルキル硫酸イオンが特に好ましい。

【0038】上記一般式 (VI) において a は 1 から 4 の整数を表す。

【0039】上記一般式 (VII) において Q は酸素原子又は窒素原子を表す。T 及び W は二価の連結基を表し、例えばエチレン基、1, 4-シクロヘキシレン基、 $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ 、 $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ 、及びフェニレン基を表す。b は 0 又は 1 を表す。

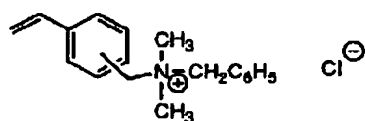
【0040】上記一般式 (VIII) 及び (IX) において R<sub>12</sub> は水素原子、脂肪族基 (例えばメチル基、t-ブチル基等)、芳香族基 (例えばフェニル基等)、ハロゲン原子、シアノ基、アシル基 (例えばアセチル基、ベンゾイル基等)、オキシカルボニル基 (例えばメトキシカルボニル基等)、アミノカルボニル基 (例えばアミノカルボニル基等)、ニトロ基等の基を表す。

【0041】上記一般式 (I) において、(A) で表さ

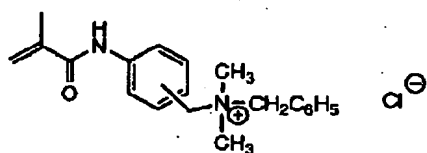
50

れるモノマー単位に導かれるモノマーの例示化合物を以下に示す。

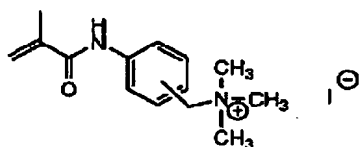
(A-1)



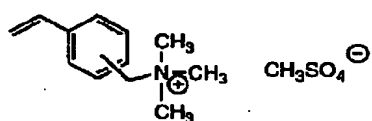
(A-3)



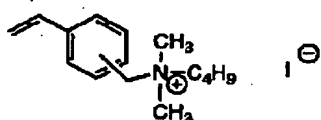
(A-5)



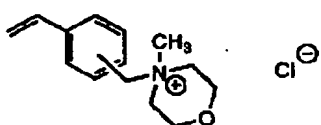
(A-7)



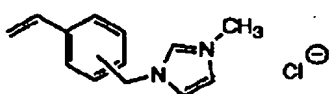
(A-9)



(A-11)



(A-13)

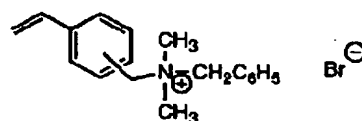


【0043】上記一般式 (I) において、(B) は以下の一般式 (X)、(XI)、及び (XII) で表されるモノマー単位が好ましい。

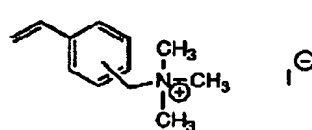
【0042】

【化8】

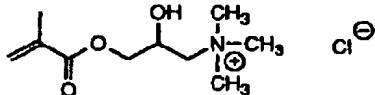
(A-2)



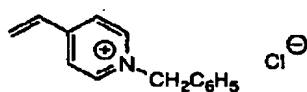
(A-4)



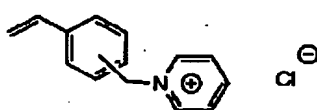
(A-6)



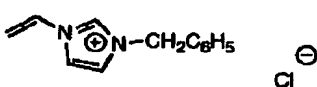
(A-8)



(A-10)



(A-12)



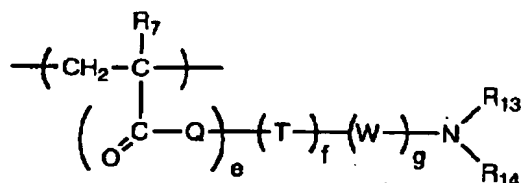
【0044】

【化9】

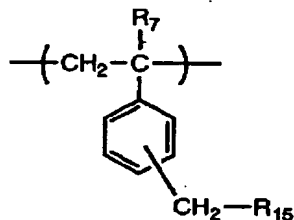
15

16

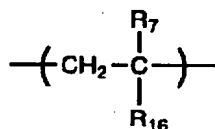
## 一般式〔X〕



## 一般式〔XI〕



## 一般式〔XII〕



【0045】上記一般式（X）、（XI）及び（XII）においてR<sub>7</sub>は水素原子又は炭素原子数1から4の脂肪族基（例えばメチル基、エチル基、n-ブチル基等）を表す。R<sub>7</sub>としては水素原子又はメチル基が好ましい。

【0046】上記一般式（X）においてQは酸素原子又は窒素原子を表す。T及びWは二価の連結基を表し、例えばエチレン基、1, 4-シクロヘキシレン基、 $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ 、 $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ 、及びフェニレン基を表す。e、f、及びgはそれぞれ0又は1を表す（但し、eが1のとき、f及びgが共に0であることはない）。R<sub>13</sub>及びR<sub>14</sub>は水素原子、アルキル基、及びアリール基を表す。これらR<sub>13</sub>及びR<sub>14</sub>で表されるアルキル基及びアリール基が

互いに結合し環状構造を形成しても良い。

【0047】上記一般式（XI）においてR<sub>15</sub>はハロゲン原子（例えば塩素原子）、芳香族基（例えばフェニル基）、アリールオキシ基（例えばフェノキシ基）、及びヒドロキシ基等を表す。

【0048】上記一般式（XII）においてR<sub>16</sub>は2-ピリジル基、4-ピリジル基、及び1-イミダゾル基を表す。

【0049】上記一般式（I）において、（B）で表されるモノマー単位に導かれるモノマーの例示化合物を以下に示す。

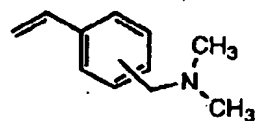
【0050】

【化10】

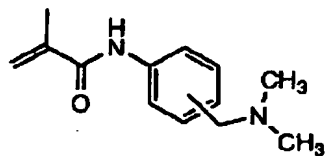


17

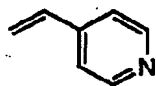
B-1



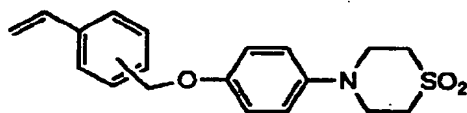
B-3



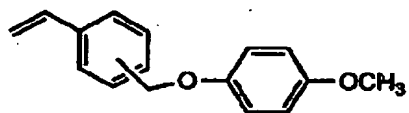
B-5



B-7

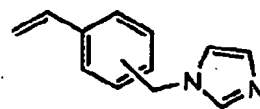


B-9

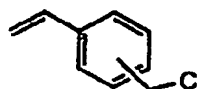


18

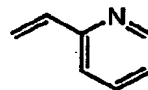
B-2



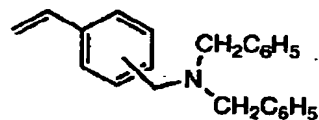
B-4



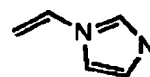
B-6



B-8



B-10



【0051】上記一般式 (I) において、(C) で表されるモノマー単位に導かれるモノマーとしては例えばジビニルベンゼン、エチレングリコールメタクリレート、エチレングリコールアクリレート、ヒドロキノンメタクリレート、ヒドロキノンアクリレート、エチレンジメタクリルアミド、エチレンジアクリルアミド、等が挙げら

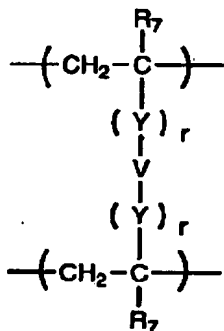
れる。

【0052】上記一般式 (I) において、(C) は以下の一般式 (XIII) で表されるモノマー単位が好ましい。

【0053】

【化11】

## 一般式 (XII)



【0054】上記一般式 (XIII) において  $R_7$  は水素原子又は炭素原子数 1 から 4 の脂肪族基 (例えばメチル基、エチル基、 $n$ -ブチル基等) を表す。 $R_7$  としては水素原子又はメチル基が好ましい。また  $V$  は二価の連結基を表し、例えばアリーレン基 (例えばフェニレン基、ナフチレン基等) 及びアルキレン基 (例えばメチレン基、1, 4-ブチレン基等) を表す。 $Y$  はエステル結合 (例えば  $-\text{C}(=\text{O})-\text{O}-$ 、 $-\text{O}-\text{C}(=\text{O})-$ )、アミド結合 (例えば  $-\text{C}(=\text{O})-\text{NH}-$ 、 $-\text{NH}-\text{C}(=\text{O})-$ 、 $-\text{SO}_2-\text{NH}-$ )、エーテル結合 ( $-\text{O}-$ ) 等を表し、 $r$  は 0 又は 1 を表す。

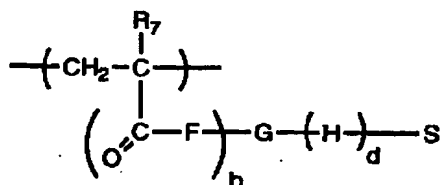
【0055】上記一般式 (I) において、(D) で表されるモノマー単位としては、例えばエチレン、プロピレン、1-ブテン、イソブテン、スチレン、 $\alpha$ -メチルスチレン、ビニルトルエン、アクリル酸及びそのエステルあるいはアミド誘導体 (例えばアクリル酸メチル、アクリル酸ブチル、 $t$ -ブチルアクリルアミド等)、メタクリル酸及びそのエステルあるいはアミド誘導体 (例えばメタクリル酸メチル、メタクリル酸ベンジル、 $n$ -ブチルメタクリルアミド等)、アクリロニトリル、メタクリロニトリル等が挙げられる。

【0056】上記一般式 (I) において、(E) は以下の一般式 (XIV) で表されるモノマー単位が好ましい。

【0057】

【化12】

## 一般式 (XIV)



【0058】上記一般式 (XIV) において  $R_1$  は水素原子又は炭素原子数 1 から 4 の脂肪族基 (例えばメチル基、エチル基、 $n$ -ブチル基等) を表す。 $R_1$  としては水素原子又はメチル基が好ましい。 $F$  は  $-\text{O}-$  又は  $-\text{N}(\text{R})-$  (式中  $R$  は水素原子、アルキル基、あるいはアリール基を表す) を表し、 $b$  は 0 又は 1 を表す。

【0059】上記一般式 (XIV) において  $G$  及び  $H$  は二価の連結基を表し、例えばメチレン基、エチレン基、1, 4-シクロヘキシレン基、 $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ 、及びフェニレン基等が挙げられる。 $d$  は 0、または 1 から 3 の整数を表す。

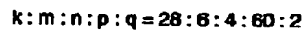
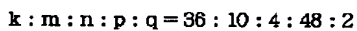
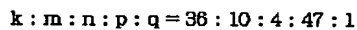
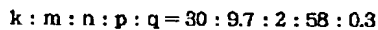
【0060】上記一般式 (XIV) において  $S$  は本発明に用いられる無機微粒子と共有結合を形成しうる基を表し、例えば  $-\text{SiX}_3$  で表される基を挙げることができる。(式中、 $X$  はハロゲン原子 (例えば塩素原子)、 $-\text{OR}$  (式中、 $R$  は水素原子、メトキシ基及びエトキシ基等のアルコキシ基、アセトキシ基及びベンゾイルオキシ基等のアシルオキシ基を表す)、 $-\text{NRR}'$  (式中、 $R$  及び  $R'$  は水素原子、メチル基及び  $t$ -ブチル基等のアルキル基、フェニル基等のアリール基を表す) 等の基を表す。)

本発明において用いられる有機カチオン性ポリマーの例示化合物を以下に示すが、本発明はこれに限定されるものではない。尚、例示したポリマーはそれぞれ下記の繰り返し単位を下記の割合で含む。

【0061】

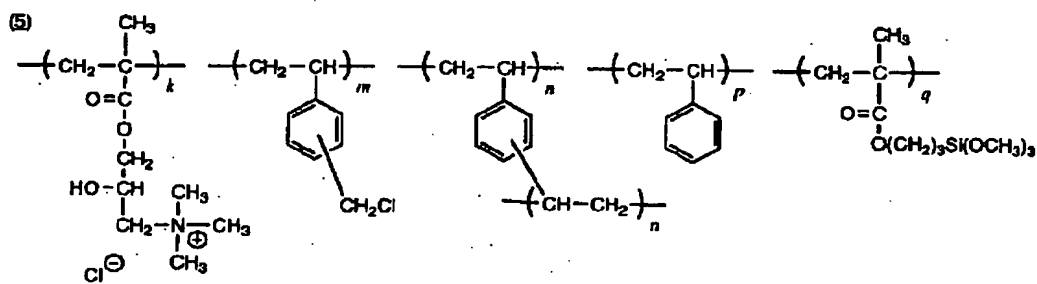
【化13】

22

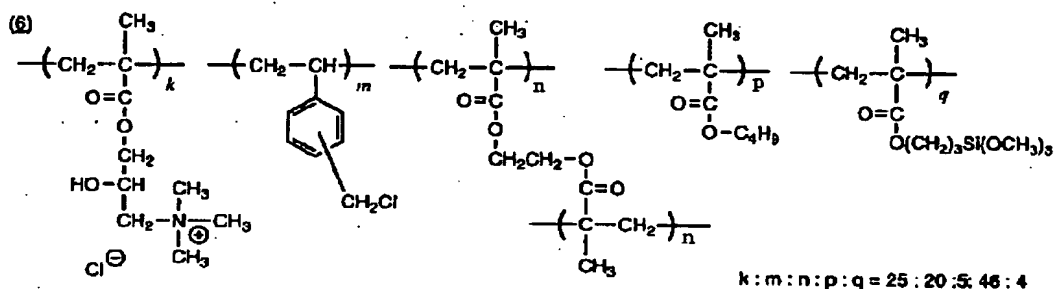


23

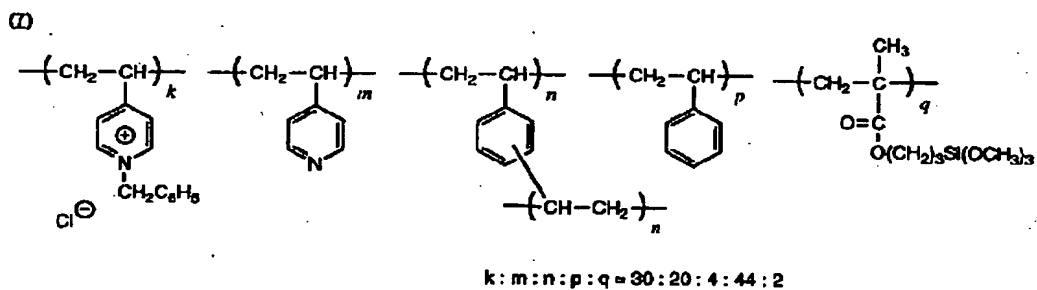
24



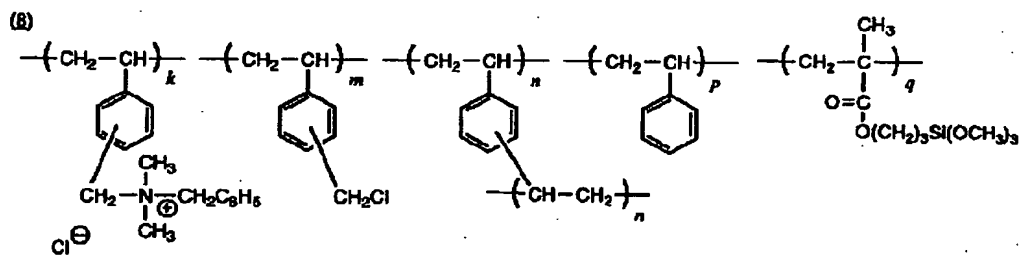
$$k:m:n:p:q = 25:10:5:55:5$$



$$k:m:n:p:q = 25:20:5:46:4$$



$$k:m:n:p:q = 30:20:4:44:2$$



$$k:m:n:p:q = 30:10:4:55:1$$

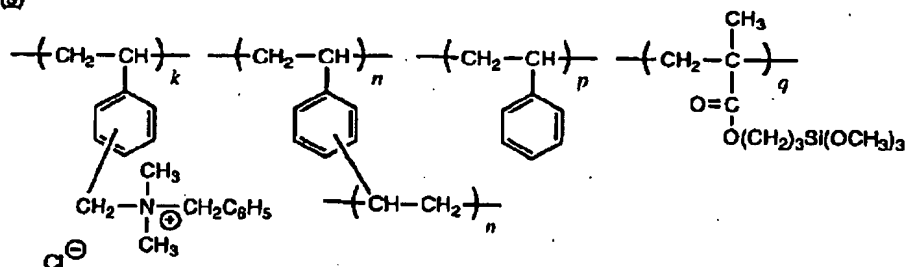
【0063】

【化15】

25

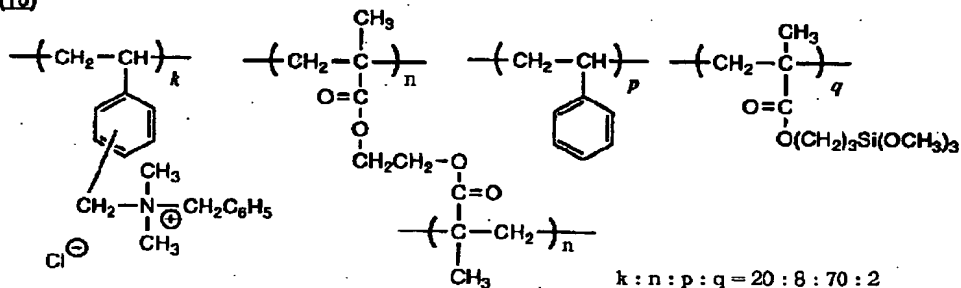
26

(9)



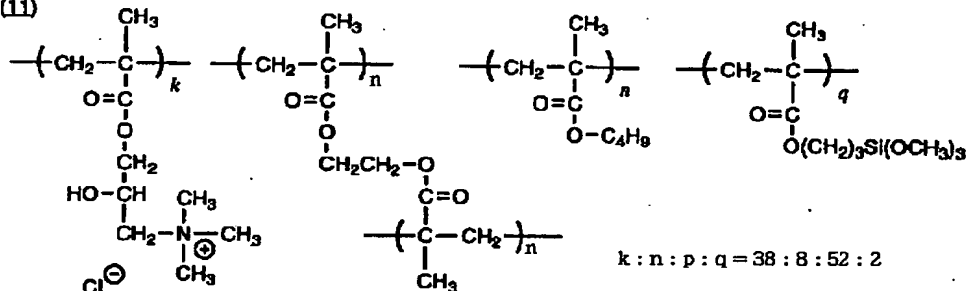
$$k : n : p : q = 30 : 6 : 62 : 2$$

(10)



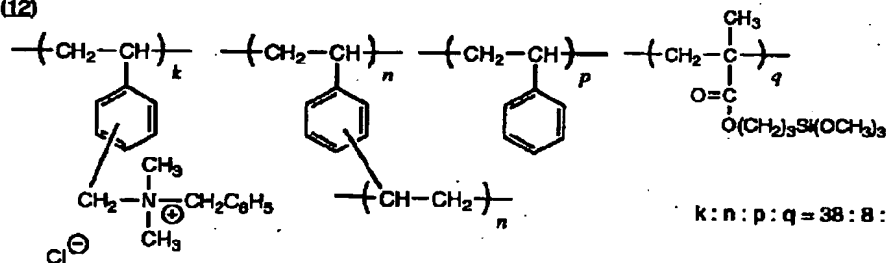
$$k : n : p : q = 20 : 8 : 70 : 2$$

(11)



$$k : n : p : q = 38 : 8 : 52 : 2$$

(12)



$$k : n : p : q = 38 : 8 : 52 : 2$$

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【0064】本発明において用いられる有機カチオン性ポリマーが結合した無機微粒子は、例えば以下に挙げる方法により合成することができる：(1) 無機微粒子表面上に重合開始基を導入しておき、表面上で重合反応を行うことにより結合させる方法、(2) 無機微粒子表面上に共重合性基あるいは連鎖移動基を導入しておき、表面上で重合反応を行うことにより結合させる方法、

(3) カチオン性の重合開始剤を無機微粒子表面上へ吸着させておき、表面近傍で重合反応を行うことにより結合させる方法、(4) ビニル基を持つ親水性マクロマー

を無機微粒子表面上へ吸着させておき、表面上で重合反応を行うことにより結合させる方法、(5) あらかじめカップリング剤をポリマー中に導入した有機ポリマーを合成しておいてから無機微粒子と結合させる方法、等。これらの方法は例えば繊維学会誌、第49巻、130～136ページに記載の報文、および表面、第28巻、285～298ページに記載の報文等に詳細に説明されている。

【0065】次に本発明で好ましく用いられる水溶性バインダー及び又はゼラチンについて説明する。

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【0066】本発明に好ましく用いられるゼラチンとしては、動物のコラーゲンを原料としたゼラチンであればいずれでも使用できるが、豚皮、牛皮、牛骨を原料としたコラーゲンを原料としたゼラチンがより好ましい。更にゼラチンの種類としては特に制限はないが、石灰処理ゼラチン、酸処理ゼラチン、誘導体ゼラチン（例えば特公昭38-4854号、同39-5514号、同40-12237号、同42-26345号、米国特許2,525,753号、同2,594,293号、同2,614,928号、同2,763,639号、同3,118,766号、同3,132,945号、同3,186,846号、同3,312,553号、英国特許861,414号、同103,189号等に記載の誘導体ゼラチン）を単独又はそれらを組み合わせて用いることができる。酸処理ゼラチンを用いると、耐水性の点で特に有利である。

【0067】本発明の受容層に含まれるゼラチンの塗工量としては、固形分として3~20 g/m<sup>2</sup>が好ましく、更に好ましくは5~15 g/m<sup>2</sup>である。

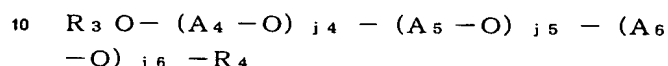
【0068】本発明で好ましく用いられる水溶性ポリマーとしては例えば、ポリビニルアルコール類、ポリビニルピロリドン類、ポリビニルピリジニウムハライド、各種変性ポリビニルアルコール等のビニルホルマール及びその誘導体（特開昭60-145879号、同60-220750号、同61-143177号、同61-235182号、同61-235183号、同61-237681号、同61-261089号参照）、ポリアクリルアミド、ポリジメチルアクリルアミド、ポリジメチルアミノアクリレート、ポリアクリル酸ソーダ、アクリル酸メタクリル酸共重合体塩、ポリメタクリル酸ソーダ、アクリル酸ビニルアルコール共重合体塩等のアクリル基を含むポリマー（特開昭60-168651号、同62-9988号等に記載）、澱粉、酸化澱粉、カルボキシ澱粉、ジアルデヒド澱粉、カチオン化澱粉、デキストリン、アルギン酸ソーダ、アラビアゴム、カゼイン、プルラン、デキストラン、メチルセルロース、エチルセルロース、カルボキシメチルセルロース、ヒドロキシプロピルセルロース等の天然高分子材料又はその誘導体（特開昭59-174382号、同60-262685号、同61-143177号、同61-181679号、同61-193879号、同61-287782号等に記載）、ポリエチレングリコール、ポリプロピレングリコール、ポリビニルエーテル、ポリグリセリン、マレイン酸アルキルビニルエーテル共重合体、マレイン酸-N-ビニルピロール共重合体、スチレン-無水マレイン酸共重合体、ポリエチレンイミン等の合成ポリマー（特開昭61-32787号、同61-237680号、同61-277483号等に記載）等を挙げることができる。これらのポリマーのうち好ましくはポリビニルピロリドン類、ポリビニルアルコール類、ポリアルキレンオキサ

イド類である。

【0069】上記ポリビニルアルコール類としては、重合度が200~4000が好ましく、特に好ましくは1000~3000の範囲である。

【0070】上記ポリアルキレンオキサイド類と、例えばポリエチレンオキサイド類、ポリエチレングリコール類、ポリプロピレングリコール類又は下記一般式（P）で示される化合物等が挙げられる。

【0071】一般式（P）



式中、A<sub>4</sub>、A<sub>5</sub>、A<sub>6</sub>はそれぞれ置換、無置換の直鎖又は分岐のアルキレン基を表すが、すべてが同一となることはない。R<sub>3</sub>、R<sub>4</sub>はそれぞれ同一であっても異なっても良く、水素原子、それぞれ置換、無置換のアルキル基、アリール基、アシル基等を表す。

【0072】それぞれの置換基としては、ヒドロキシ基、カルボキシ基、スルホニル基、アルコキシ基、カルバモイル基、スルファモイル基が挙げられる。好ましくは、R<sub>3</sub>、R<sub>4</sub>が水素原子であり、A<sub>4</sub>、A<sub>5</sub>、A<sub>6</sub>がそれぞれ無置換のものである。また最も好ましいものとしては、A<sub>4</sub>、A<sub>5</sub>、A<sub>6</sub>が-CH<sub>2</sub>CH<sub>2</sub>-又は-CH(CH<sub>3</sub>)-CH<sub>2</sub>である。

【0073】j<sub>4</sub>、j<sub>5</sub>、j<sub>6</sub>は、それぞれ0又は1~500の整数を表す。但し、j<sub>4</sub>+j<sub>5</sub>+j<sub>6</sub>≧5である。

【0074】ポリアルキレンオキサイド類で好ましいものとしてはポリエチレンオキサイド類であり、平均分子量が10,000~500,000の範囲にあるものが好ましく、特に好ましくはポリエチレングリコール（PEGと称することもある）で、平均分子量が50,000~300,000の範囲のものである。

【0075】上記ポリアルキレンオキサイド類の平均分子量は水酸基価により算出した分子量である。

【0076】本発明において、水溶性ポリマーを架橋する目的として本発明に影響しない範囲で架橋剤を適用することが好ましい。架橋剤の具体的な例としては、ホルムアルデヒド、グルタルアルデヒドの如きアルデヒド系化合物、ジアセチル、クロルペンタンジオンの如きケトン化合物、ビス（2-クロロエチル尿素）、2-ヒドロキシ-4,6-ジクロロ-1,3,5-トリアジン等のトリアジン系化合物、米国特許3,288,775号記載の如き反応性のハロゲンを有する化合物、ジビニルスルホン、特開平8-50342号記載のカルバモイルピリジニウム系化合物、米国特許3,635,718号記載の如き反応性のオレフィンをもつ化合物、米国特許2,732,316号記載のN-メチロール化合物、米国特許3,103,437記載の如きイソシアナート類、米国特許3,017,280号、同2,983,611号記載の如きアジリジン化合物類、米国特許3,1

00, 704号記載の如きカルボジイミド系化合物類、米国特許3, 091, 537号記載の如きエポキシ化合物、ムコクロル酸の如きハロゲンカルボキシルアルデヒド類、ジヒドロキシジオキサンの如きジオキサン誘導体等の有機架橋剤、クロム明ばん、カリ明ばん、硫酸ジルコニウム、ほう酸等無機架橋剤等があり、これらを1種又は2種以上組み合わせて用いることができる。

【0077】本発明の受容層を形成する方法としては、サイズプレス法、ロールコーター法、ブレードコーター法、エアナイフコーター法、ゲートロールコーター法、ロッドバーコーター法、カーテン法、スライドホッパー法、エクストルージョン法等、通常用いられている塗工方法が用いられる。

【0078】本発明の受容層には、更に、バインダ、硬膜剤の他、無機顔料、着色染料、着色顔料、インク染料の定着剤、紫外線吸収剤、酸化防止剤、顔料の分散剤、消泡剤、レベリング剤、防腐剤、蛍光増白剤、粘度安定剤、pH調節剤等の公知の各種添加剤を添加することもできる。

【0079】本発明の受容層には画質を向上させる目的で、インク吸収性を損なわない範囲で界面活性剤を添加することが好ましい。用いられる界面活性剤はアニオン系、カチオン系、ノニオン系、ベタイン系のいずれもタイプでもよく、また低分子のものでも高分子のものでも、異なる種類のものを併用してもよい。これらの中で好ましくはフッ素系の界面活性剤である。

【0080】上記フッ素系界面活性剤は、例えば米国特許2, 559, 751号、同2, 567, 011号、同2, 732, 398号、同2, 764, 602号、同2, 806, 866号、同2, 809, 998号、同2, 915, 376号、同2, 915, 528号、同2, 918, 501号、同2, 934, 450号、同2, 937, 098号、同2, 957, 031号、同3, 472, 894号、同3, 555, 089号、英国特許1, 143, 927号、同1, 130, 822号、特公昭45-37304号、特開昭47-9613号、同49-134614号、同50-117705号、同50-117727号、同50-121243号、同52-41182号、同51-12392号、英国化学会誌(J. Chem. Soc.) 1950年2789頁、同1957年2574頁及び2640頁、米国化学会誌(J. Amer. Chem. Soc.) 79巻2549頁(1957年)、油化学(J. Japan Oil Chemists Soc.) 12巻653頁、有機化学会誌(J. Org. Chem.) 30巻3524頁(1965年)等に記載された方法によって合成することができる。

【0081】これらのフッ素系界面活性剤のうち、ある種のものは大日本インキ化学工業社からメガファック(Megafac) Fなる商品名で、ミネソタ・マイニ

ング・アンド・マニファクチュアリング・カンパニー社からフルオラッド(Fluorad) FCなる商品名で、インペリアル・ケミカル・インダストリー社からモンフロール(Monfleur)なる商品名で、イー・アイ・デュポン・ネメラス・アンド・カンパニー社からゾニルス(Zonyls)なる商品名で、又、ファルペベルケ・ヘキスト社からリコベット(Licowet) VPFなる商品名で、それぞれ市販されている。

【0082】本発明の受容層の塗工量としては5~100 g/m<sup>2</sup>が好ましく、より好ましくは10~50 g/m<sup>2</sup>である。また受容層の厚みとしては10~100 μmであることが好ましく、特に好ましくは40~70 μmの範囲である。

【0083】インク受容層中には、搬送性を向上させる目的で有機マツト剤を使用することができる。

【0084】マツト剤は、写真技術分野においてよく知られており、親水性有機コロイドバインダー中に分散可能な有機材料の不連続固体粒子であると定義できる。

【0085】有機マツト剤の例としては澱粉、セルロースエステル(例えば、セルロースアセテートプロピオネート等)、セルロースエーテル(例えばエチルセルロース等)、合成樹脂等である。合成樹脂の例としては、水不溶又は難溶性合成ポリマーであり、例えばアルキル(メタ)アクリレート、アルコキシアルキル(メタ)アクリレート、グリシジル(メタ)アクリレート、(メタ)アクリルアミド、ビニルエステル(例えば酢酸ビニル)、アクリロニトリル、オレフィン(例えばエチレン等)、スチレン、ベンゾグアナミン・ホルムアルデヒド縮合物等の単独若しくは組み合わせ、又はこれらとアクリル酸、メタクリル酸、α, β-不飽和ジカルボン酸、ヒドロキシアルキル(メタ)アクリレート、スルホアルキル(メタ)アクリレート、スチレンスルホン酸等の組み合わせを単量体成分とするポリマーを用いることができる。

【0086】その他エポキシ樹脂、ナイロン、ポリカーボネート、フェノール樹脂、ポリビニルカルバゾール、ポリ塩化ビニリデン等も用いることができる。

【0087】これらマツト剤は、搬送性の観点から、重量平均粒径が3~20 μmが好ましく、かつ受容層中の総重量(付き量ともいう)は10~100 mg/m<sup>2</sup>であることが好ましく、塗工液安定性の点から、3 μm以下の粒子や、20 μm以上の粒子を分級により予め排除しておくことが好ましい。また、これらマツト剤は併用することも可能である。

【0088】本発明に係るインクジェットプリンター用記録用紙とは、紙に限らず、いわゆるインクジェット記録材の全てを意味しており、記録材とは、支持体上に塗工するか、含有させたものをさし、支持体としては、シート状、板状だけでなく、缶の表面などのようなものなど特に制限無く利用できる。また、透明な支持体でも不

透明な支持体でも使用目的に応じて用いることができる。

【0089】透明な支持体としては、従来公知のものがいずれも使用でき、例えば、ポリエステル樹脂、セルロースアセテート樹脂、アクリル樹脂、ポリカーボネート樹脂、ポリ塩化ビニール樹脂、ポリイミド樹脂、セロファン、セルロイドなどのフィルムないしシートあるいはガラス板などがある。これらの中で支持体の剛性、透明性の観点からポリエステル樹脂、特にポリエチレンテレフタレートフィルムが好ましい。

【0090】不透明な支持体としては、上質紙、中質紙、スーパーカンレンダー処理紙、片艶原紙、トレーシングペーパー等の非塗工紙、アート紙、コート紙、軽量コート紙、微塗工紙、キャストコート紙等の塗工紙、プラスチックフィルム、顔料入り不透明フィルム、発泡フィルム等のフィルム、樹脂被覆紙、樹脂含浸紙、不織布、布、金属フィルム、金属板など、およびこれらの複合体を用いることができる。

【0091】これらの中で、光沢性、平滑性の観点から樹脂被覆紙、各種フィルムが好ましく、手触り感、高級感から樹脂被覆紙ではポリオレフィン樹脂被覆紙、また各種フィルムでは、ポリエステル系のフィルムがより好ましい。

【0092】好ましく用いられる樹脂被覆紙を構成する原紙は、特に制限はなく、一般に用いられている紙が使用できるが、より好ましくは例えば写真用支持体に用いられているような平滑な原紙が好ましい。原紙を構成するパルプとしては天然パルプ、再生パルプ、合成パルプ等を1種もしくは2種以上混合して用いられる。この原紙には一般に製紙で用いられているサイズ剤、紙力増強剤、填料、帯電防止剤、蛍光増白剤、染料等の添加剤が配合される。

【0093】更に、表面サイズ剤、表面紙力剤、蛍光増白剤、帯電防止剤、染料、アンカー剤等が表面に塗布されていてもよい。

【0094】又、原紙の厚みに関しては特に制限はないが、紙を抄造中又は抄造後カレンダー等にて圧力を印加して圧縮するなどした表面平滑性の良いものが好ましい。

【0095】樹脂被覆紙の樹脂としては、ポリオレフィン樹脂や電子線で硬化する樹脂を用いることができる。ポリオレフィン樹脂としては、低密度ポリエチレン、高密度ポリエチレン、ポリプロピレン、ポリブテン、ポリペンテン等のオレフィンのホモポリマー又はエチレン-プロピレン共重合体などのオレフィンの2つ以上からなる共重合体及びこれらの混合物であり、各種の密度、各種の熔融粘度指数（メルトインデックス）のものを単独あるいはそれらを混合して使用できる。

【0096】又、樹脂被覆紙の樹脂中には、酸化チタン、酸化亜鉛、タルク、炭酸カルシウム等の白色顔料、

ステアリン酸アミド、アラキジン酸アミドなどの脂肪酸アミド、ステアリン酸亜鉛、ステアリン酸カルシウム、ステアリン酸アルミニウム、ステアリン酸マグネシウムなどの脂肪酸金属塩、イルガノックス1010、イルガノックス1076などの酸化防止剤、コバルトブルー、群青、セシリアンブルー、フタロシアニンブルーなどのブルーの顔料や染料、コバルトバイオレット、ファストバイオレット、マンガン紫などのマゼンタの顔料や染料、蛍光増白剤、紫外線吸収剤などの各種の添加剤を適宜組み合わせる加えるのが好ましい。

【0097】本発明で用いられる支持体はJIS P-8125によるテーパー剛度が1~15 g・cmのものが温湿度の環境変化に対して、連続搬送性が向上するため特に好ましく使用される。

【0098】本発明のインクジェット記録方法は、①5種以上の異なるインクを使用して出力する記録装置で、本発明の記録材に記録すること、②少なくとも1種の基準色に対して、2種以上の異なるインクにより記録する記録装置で、本発明の記録材に記録すること、又は③前記基準色が、該基準色のインクの吸光度が実質的に異なる2種以上のインクにより記録する記録装置で記録することを特徴とする。

【0099】本発明に使用されるインクジェット記録方法は、例えば水を40重量%以上含有するインクで本発明のインクジェット用記録シートに記録するインクジェット記録方法が好ましく用いられ、該インクに下記の着色剤、液媒体、その他の添加剤からなるインクジェット記録液体が用いられる。着色剤としては、直接染料、酸性染料、塩基性染料、反応性染料あるいは食品用色素等の水溶性染料が挙げられる。

【0100】本発明の受容層に用いられるインクの溶媒としては、水及び水溶性の各種有機溶剤、例えば、メチルアルコール、エチルアルコール、プロピルアルコール、イソプロピルアルコール、ブチルアルコール、sec-ブチルアルコール、tert-ブチルアルコール、イソブチルアルコール等の炭素数1~4のアルキルアルコール類；ジメチルホルムアミド、ジメチルアセトアミド等のアミド類；アセトン、ジアセトンアルコール等のケトン又はケトンアルコール類；テトラヒドロフラン、ジオキサン等のエーテル類；ポリエチレングリコール、ポリプロピレングリコール等のポリアルキレングリコール類；エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1, 2, 6-ヘキサントリオール、チオジグリコール、ヘキシレングリコール、ジエチレングリコール等のアルキレン基が2~6個のアルキレングリコール類；グリセリン、エチレングリコールメチルエーテル、ジエチレングリコールメチル（又はエチル）エーテル、トリエチレングリコール、モノメチルエーテル等の多価アルコールの低級アルキルエーテル類、2H-ピロリジノン等のピロリジノ



ン類、1-メチル-2-ピロリドン、2-ピロリドン等のピロリドン類等が挙げられる。これらの多くの水溶性有機溶剤の中でも、ジエチレングリコール等の多価アルコール、トリエチレングリコールモノメチルエーテル、トリエチレングリコールモノエチルエーテル等の多価アルコールの低級アルキルエーテル、ピロリドン類が好ましい。

【0101】インクの溶媒はインクヘッドノズルの目詰り防止の観点から水と前記有機溶媒の混合溶媒を用いることが好ましいが、この時、水のインクに対する含有量は40重量%以上であり、好ましくは50～90重量%である。

【0102】その他のインクへの添加剤としては、例えば、pH調節剤、金属封鎖剤、防カビ剤、粘度調整剤、表面張力調整剤、湿潤剤、界面活性剤及び防錆剤等が挙げられる。

【0103】また、本発明においては、濃淡インクを使用した記録装置で記録すると、本発明の効果が顕著に現れる。例えば、従来のカラー記録装置は、Y、M、C、Kの4つの基準色に対して、各1種類のインクを使用する方法が主流であるが、ある基準色については2種以上のインクを使用した場合、多階調化や、低濃度部のざらつき感を向上できる。特にある基準色（例えばY、M、C、K）が2種類以上の吸光度の異なるインク（濃淡インク）を使用することであり、低濃度部は主として淡色（吸光度の低い）のインクを使用しざらつき感を低減し、また、高濃度部は主として濃色（吸光度の高い）のインクを使用し、十分な最大濃度が出るような構成が知られている。淡色インクと濃色インクが同じ染料を使用しているにもかかわらず、異なる染料を使用しているにもかかわらず、複数の異なる染料の組み合わせなどでも構わない。このような基準色について濃淡インクを使用している記録装置としては、PM-700C（セイコーエプソン）、Picty 300（NEC）、Photo Smart（ヒューレットパカード）の商品名で市販されており、Y、M、C、Kのほかに淡色のM、淡色のCのインクの計6種のインクにより出力することが特徴である。また、同様の方式の記録装置の例としてBJC-700J（キャノン社製）も挙げられる。

#### 【0104】

【実施例】以下、実施例によって本発明を更に詳細に説明するが、本発明はこれらに限定されるものではない。

【0105】＜支持体の作製＞坪量60g/m<sup>2</sup>の基材の表面に低密度ポリエチレン70部と高密度ポリエチレン20部からなる樹脂組成物を20g/m<sup>2</sup>塗工し、裏面に低密度ポリエチレン50部からなる樹脂組成物を20g/m<sup>2</sup>塗工した支持体を作製した。

【0106】＜有機カチオン性ポリマーが結合した無機微粒子（ポリマー結合無機微粒子）の合成＞

（1）表面処理されたコロイダルシリカの合成

300mlの四つ口フラスコに攪拌機を装着し、コロイダルシリカ（商品名スノーテックスOUP、日産化学社製）を100g（シリカの含有量は20%）を投入した。これに3-メタクリロキシプロピルトリメトキシシランを1.0g、蒸留水を10g、攪拌しながら滴下した。さらに室温で30分反応させ、目的とする表面処理されたコロイダルシリカを分散物として得た。

#### 【0107】（2）中間体微粒子の合成

2リットルの四つ口フラスコに攪拌機、温度計、ガス導入管、コンデンサーを装着し、蒸留水を200g、界面活性剤（商品名トラックスH-45）を7.7g、水酸化カリウムを0.78gを投入した。窒素ガスを流しながら室温で30分間攪拌し、脱気した。これにスチレンを12.1g、ジビニルベンゼンを0.8g、ジメチルアミノメチルスチレンを12.9gを投入し、さらに上記（1）で表面処理したコロイダルシリカの分散液を13.7g加えた。毎分300回転で攪拌しながら内温が70℃になるまで加熱し、その後2, 2'-アゾビス（イソシアノ吉草酸）を0.84g添加した。そのまま5時間、窒素気流下で加熱攪拌を行い、重合させた。

【0108】反応終了後、グラスフィルターを用いて不要な固形分を除去した後、目的とする中間体微粒子を乳白色分散物として得た。

#### 【0109】（3）ポリマー結合無機微粒子（1）の合成

300mlの四つ口フラスコに攪拌機を装着し、上記（2）で合成した中間体微粒子を100g投入した。これにアセトニトリル30mlを30分間かけて攪拌しながら滴下した。さらに塩化ベンジルを3.1g滴下し、60℃の油浴中で6時間加熱攪拌した。反応終了後、室温まで放冷した後、減圧下溶媒を約40ml溜留した。残った液体に蒸留水を加え、全体を100gに調整して目的とするポリマー結合無機微粒子（1）を乳白色分散物として得た。

【0110】（4）表面処理される無機微粒子を表1記載の化合物にすると共に各モノマーの比率を例示化合物中記載の値にした他は同様の操作により例示化合物（2）、（3）、（4）、（7）、（8）、（10）を母核にもつポリマー結合無機微粒子（1）、（2）、（3）、（4）、（7）、（8）、（10）を合成した。

#### 【0111】実施例1～13

上記方法により作成されたポリマー結合無機微粒子（1）、（2）、（3）、（4）、（7）、（8）、（10）を88重量部、ケン化度98%ポリビニルアルコール重合度2500（以下単にPVAと称することもある）を12重量部添加した塗工液を作成し、ワイヤーバーにて乾燥固形分が20g/m<sup>2</sup>となるように塗工し、試料を作成した。

#### 【0112】比較例1～3

コロイダルシリカ、アルミナゾル、酸化亜鉛をそれぞれ88重量部、ケン化度98%ポリビニルアルコール重合度2500を12重量部添加した塗工液を作成し、ワイヤーバーにて乾燥固形分が20g/m<sup>2</sup>となるように塗工し、試料を作成した。

#### 【0113】比較例4

polymer journal, vol. 21, No. 6, p475 (1989) や、Journal of polymer science, A, vol. 29, p697 (1992) や、表面, vol. 30, No. 1, p74 (1992) 等に記載の方法にしたがって、シリカを核としてアクリレートをグラフト化した無機微粒子を作成した。その後、作成した無機微粒子を88重量部、ケン化度98%ポリビニルアルコール重合度2500を12重量部添加した塗工液を作成し、ワイヤーバーにて乾燥固形分が20g/m<sup>2</sup>となるように塗工し、試料を作成した。

【0114】次に上記実施例1～13及び比較例1～4で作成した試料を以下の方法により、評価を行った。この時すべての評価はセイコーエプソン社製インクジェットプリンターPM700Cを用いて出力した。また、この時の出力環境としては、クラックの発生を除き梅雨時期を想定し、25℃、70%RHの環境で行った。

【0115】<クラックの発生>得られた試料を210mm×297mm(A4)に裁断し、内径30mmの筒状となるように長手方向に丸め、テープで止めた試料を10本作製し、15℃、20%環境に1週間放置した。その後、1枚につき5、6カ所ランダムに10mm×10mm範囲を決定し、亀裂の個数を光学顕微鏡にて測定し、A4、1枚あたり平均亀裂数をクラック数とした。

【0116】<ブリーディング>SCID N3画像を印字し、シアン-マゼンタ、マゼンタ-イエロー、イエロー-シアンのドットの重なりを光学顕微鏡にて観察した。

◎;色濁りは殆ど観察されず、鮮鋭性も高い画像が得られた。

○;シアン-マゼンタ部分にのみ多少の色濁りが生じるが、画像は問題ないレベル。

△;シアン-マゼンタ、マゼンタ-イエロー部分に色濁りがあり、画像の赤色部分がムラ状に見える。

×;全色で色濁りが生じており、全体的にぼやけた画像になった。

【0117】<ビーディング>イエロー、マゼンタ、シアン、ブラック、グリーン、ブルー、レッドの最高濃度部を出力し、ざらつき度合いを目視にて評価した。

◎;各色ともに全くざらつきが無く、優れている。

○;グリーン部にわずかなざらつきが確認されるが実害レベルではない。

△;グリーン部とブルー部にざらつきが確認される。

×;全体的にざらつきが酷く、商品レベルにならない。

【0118】<乾燥性>A4サイズの自然画像を出力し、10分後に用紙を内径4cmとなるように丸め、テープで止めた後、1日後に試料を観察し、裏面の転写度合いを目視にて評価した。

【0119】◎;全く転写無し。

○;わずかに転写があるが実技上問題なし。

△;高濃度部において転写が発生する。

×;転写が発生し、転写面より膜がはがれる。

【0120】

【表1】

実施例	有機カチオン性ポリマー／無機微粒子	有機カチオン性ポリマー／無機微粒子比	受容層中の含有率(重量%)	フリーシリカ	ビーズシリカ	乾燥性	クラックの発生(個/A4サイズ)
実施例 1	エポキシ樹脂 *1	0.5/99.5	88	◎	◎~○	◎	2
実施例 2	エポキシ樹脂 *1	0.5/99.5	88	◎~○	○	◎	1
実施例 3	エポキシ樹脂 *1	0.5/99.5	88	◎~○	○	◎	2
実施例 4	エポキシ樹脂 *1	0.5/99.5	88	◎~○	○	◎	1
実施例 5	エポキシ樹脂 *1	0.5/99.5	88	◎~○	○	◎	1
実施例 6	エポキシ樹脂 *1	0.5/99.5	88	◎~○	◎~○	◎	1
実施例 7	エポキシ樹脂 *1	0.5/99.5	88	◎~○	○	◎	2
実施例 8	酸化シリカ	0.5/99.5	88	○	○	◎~○	5
実施例 9	アルミナ	0.5/99.5	88	◎	◎~○	◎	4
実施例 10	酸化亜鉛	0.5/99.5	88	○	○	○	7
実施例 11	酸化ジルコニア	0.5/99.5	88	○	○	○	7
実施例 12	非晶質シリカ *3	0.5/99.5	88	◎	◎~○	◎	1
実施例 13	酸化エチレン	0.5/99.5	88	○	○	○	8
比較例 1	エポキシ樹脂 *2	0.5/99.5	88	△	△~×	△	21
比較例 2	酸化亜鉛	0.5/99.5	88	△	△~×	△	33
比較例 3	アルミナ	0.5/99.5	88	△	△	△	20
比較例 4	エポキシ樹脂	0.5/99.5	88	○	△	△	35

コロイダルシリカ \*1 日産化学社製スノーテックスOUP

コロイダルシリカ \*2 日産化学社製スノーテックスO

非晶質シリカ \*3 日本 AEROSIL 社製 AEROSIL 200

表 1 から判るように、本発明のインクジェットプリンター用記録用紙はクラックの発生を防止し、かつ高温条件下においても乾燥性を向上させ、かつ高濃度で高精細な画像を得ることができ、良好な結果を示すことも判る。

#### 【0121】実施例 14~29

実施例 3 で使用したコロイダルシリカ（日産化学社製；スノーテックスOUP）と例示化合物 3 を用い、表 2 記載の値となるように有機カチオン性ポリマー／無機微粒子比を調整し、又、塗工液中のポリマー結合無機微粒子

の量を調整し、受容層中の含有率を表 2 記載の値となるようにした他は同様の操作により、試料を作成し、評価を行った。このとき以下の評価を追加した。

【0122】＜髭状の筋発生＞クラックの発生と同様の評価を行った後、試料の全面にアルファベット（26 文字）黒字を印刷し、文字の境界線に発生する髭状の筋を目視にて観察した。

◎；髭状の筋の発生は全く見られなかった。

○；5 カ所未満の発生は見られたが実技上全く問題ないレベル。

△；5～30カ所の発生が確認され、やや目立つレベル。

×；30カ所以上の発生が確認され、実技上問題あるレベル。

【0123】＜印字後の光沢性＞イエロー、マゼンタ、シアン、ブラック、グリーン、ブルー、レッドの最高濃度部を出力し、十分乾いた後に光沢性を目視にて確認した。

◎；各色ともに光沢性を維持している。

○；ブラック部の光沢性が若干落ちているものの、その他の色は光沢性を維持しており、実技上全く問題ないレベル。

△；全体的に若干光沢性が劣り、濃度もやや劣るレベルであるが、実害性は問題なし。

×；各色ともに光沢性が無く、問題レベル。

【0124】

【表2】

	有機物/無機微粒子比	受容層中の含有率(重量%)	フリンジング	ビーズング	乾燥性	膜上のスジ	印字部の光沢性
実施例 14	0.5/99.5	88	◎～○	○	◎	○	○
実施例 15	10/90	88	◎	◎～○	◎	◎～○	◎
実施例 16	20/80	88	◎	◎	◎	◎	◎
実施例 17	50/50	88	◎	◎	◎	◎	◎
実施例 18	80/20	88	◎	◎	◎	◎	◎
実施例 19	90/10	88	◎	◎	◎	◎	◎
実施例 20	99.5/0.5	88	○	○	○	◎～○	○
実施例 21	20/80	5	○	○	○	○	○
実施例 22	20/80	10	◎～○	◎～○	◎～○	◎～○	◎～○
実施例 23	20/80	30	◎～○	◎～○	◎～○	◎～○	◎～○
実施例 24	20/80	50	◎	◎	◎	◎	◎
実施例 25	20/80	70	◎	◎	◎	◎	◎
実施例 26	20/80	99	◎	◎	◎	◎	◎
実施例 27	20/80	100	◎～○	◎～○	◎～○	◎	◎
実施例 28	1/99	88	◎	◎～○	◎	◎～○	○
実施例 29	99/1	88	◎～○	◎～○	◎～○	◎～○	○

【0125】表2から判るように有機カチオン性ポリマー／無機微粒子比が1／99以上99／1以下のとき良

50 好な結果を示しており、又、受容層中の含有率が10～99重量%のとき更に良好な結果を示すことが判る。

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## 【0126】実施例30

実施例1～29で作成した試料を、セイコーエプソン社製インクジェットプリンターPM700Cに代えてヒューレットパッカード社製デスクジェット2000Cにて行ったが、ほぼ同様の結果が得られ、本発明の効果が十分発揮されていることが確認された。

## 【0127】

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【発明の効果】本発明によるインクジェットプリンター用記録シート等の記録材は、上述した近年急速に増加している高速、多吐出量プリンターやロールプリンターで生じている画質の劣化（ビーディング、ブリーディングなど）や乾燥性の劣化、クラックの発生や印字部と未印字部の境界に生じる髭状の筋の発生を解決する。

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